CATALYTIC UPGRADING

TECHNOLOGY AREA

CONTENTS

INTRODUCTION

The Catalytic Upgrading Technology Area is one of 12 technology areas that were reviewed during the 2021 Bioenergy Technologies Office (BETO) Project Peer Review, which took place virtually March 8–12, March 15–16, and March 22–26, 2021. A total of 20 presentations were reviewed in the Catalytic Upgrading session by five external experts from industry, academia, and other government agencies. For information about the structure, strategy, and implementation of the technology area and its relation to BETO's overall mission, please refer to the corresponding Program and Technology Area Overview presentation slide decks: https://www.energy.gov/sites/default/files/2021-04/beto-06-peer-review-2021-plenary-craig.pdf and https://www.energy.gov/eere/bioenergy/2021-project-peer-review-catalytic-upgrading.

This review addressed a total U.S. Department of Energy (DOE) investment value of approximately $45,920,419, which represents approximately 6.94% of the BETO portfolio reviewed during the 2021 Peer Review. During the Project Peer Review meeting, the presenter for each project was given 20–65 minutes to deliver a presentation and respond to questions from the Review Panel.

Projects were evaluated and scored for their project management, approach, impact, and progress and outcomes. This section of the report contains the Review Panel Summary Report, the Technology Area Programmatic Response, and the full results of the Project Peer Review, including scoring information for each project, comments from each reviewer, and the response provided by the project team.

BETO designated Mr. Trevor Smith and Dr. Sonia Hammache as the Catalytic Upgrading Technology Area review leads, with contractor support from Mr. Jesse Glover (Boston Government Services, LLC). In this capacity, Mr. Smith and Dr. Hammache were responsible for all aspects of review planning and implementation.

CATALYTIC UPGRADING REVIEW PANEL

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CATALYTIC UPGRADING REVIEW PANEL SUMMARY REPORT

Prepared by the Catalytic Upgrading Review Panel

INTRODUCTION

The Catalytic Upgrading Technology Area focuses on developing process design strategies for the conversion of biogenic carbon (e.g., bio-oils, pyrolysis oils, lignin, sugars, and various bioprocess intermediates) or atmospheric carbon (i.e., carbon dioxide, CO_2) into heat, power, transportation fuels, and chemical commodities. Technologies within this portfolio are united by their use of catalytic surface chemistry, with the bulk of the projects relying on heterogeneous (solid) catalysts to facilitate vapor-phase and/or liquid-phase transformations of biogenic, carbon-rich feedstocks. All research is directed toward reducing the minimum fuel selling price (MFSP) below $3 per gallons gasoline equivalent (GGE) in various process technologies. Innovation typically centers on the cycle of catalyst design, synthesis, characterization, and application. Specifically, continuous improvement efforts are directed toward understanding the performance of the current generation of catalysts during a development cycle and leveraging the knowledge gained to design the next generation of catalysts and processes in the new cycle. In this way, the Catalytic Upgrading Technology Area is accelerating the development and deployment of heterogenous catalytic materials and catalytic processes to address challenges in energy and resource sustainability, in line with the vision of the Materials Genome Initiative.

Attaining MFSP levels of $3/GGE is the 2022 target for projects in this technology area; in general, achieving this level of approximate cost parity with conventional, petroleum-based fuels is a grand challenge for the field. Progress made toward this goal by the Catalytic Upgrading Technology Area is noteworthy. Projects herein have systematically and continuously reduced MFSP estimates since their inception. This has been accomplished through two broad thrusts. The first thrust includes efforts that decrease residence times (reactor size), improve catalyst stability, and intensify processes. These efforts directly reduce capital expenditures (CapEx) and operating expenditures (OpEx) associated with the production of biofuels. The second thrust includes research aimed at producing high-value chemicals from sugars or underutilized lignin. These efforts generate coproduct revenue, which helps to make biofuels cost-competitive in the near term. All advances in these two thrusts have been facilitated by the development of better catalysts and intensified processes that utilize them.

Individual research programs within the Catalytic Upgrading Technology Area are diverse in scope; however, all are united in their focus on heterogeneous catalysis and their goal of reducing the MFSP for alternative transportation fuels. Projects are selected based on their potential for reducing the cost of biofuel production, and research ventures within each project are determined by the specific technology demands in that area. Broadly speaking, programs are pursuing relevant and impactful work across the board. As an example of domain-specific research, reactor technologies for upgrading bio-oils produced through catalytic fast pyrolysis (CFP) generally seek to produce hydrocarbon fuels. This forces them to compete in a low-margin transportation fuels sector; accordingly, minimizing the cost of catalysts is critical to achieving favorable process economics. With this in mind, it is appropriate that the CFP program has a strong focus on reducing noble metal utilization and improving catalyst durability. In contrast, selectivity control is often a more critical issue in the production of high-value products, such as 2,3-butanediol (BDO) or triptane (isooctane); hence, efforts in these areas focus on tuning specificity through the development of selective materials and operating conditions. A key feature of this portfolio is that many of its technologies have matured to the point where they could be transitioned to the pilot scale, so process systems integration is a crucial focus area. Specifically, catalytic processes in a downstream unit are often critically impacted by the carryover of upstream impurities, and it is appropriate that these programs—such as the furan-based platform within the Catalytic Upgrading of Biochemical Intermediates (CUBI)—are increasingly working on process integration within this technology area and through their interface with the separations consortium. This interface with separations is critically important for two reasons. First, upstream separation efficiency dictates purity specifications in feeds to the catalytic processes in this portfolio. Second, selectivities attained in processes developed in the Catalytic Upgrading Technology Area determine the extent of downstream separation and purification. In general, the more selective a catalytic process is, the less costly the downstream purification will be.

Various funding mechanisms are at work in this technology area. Projects are supported as part of the annual operating plan (AOP), through directed funding award (DFA) projects, and through funding opportunity announcements (FOAs). AOP projects comprise 75% of the portfolio. They represent core research programs at DOE national laboratories, and they span a large set of technologies that range from foundational science to translational efforts, along with crosscutting, enabling initiatives. DFA projects directly engage the private sector. This allows industry partners to leverage facilities and expertise at the national laboratories, which brings leading-edge research to bear on problems of current industrial relevance. Finally, FOA programs engage various external partners and provide an avenue for academic institutions to contribute toward reducing MFSP for bio-based fuels. Often, this is accomplished by pursuing high-reward, lower-technology-readiness-level (TRL) strategies that stand to significantly contribute toward BETO goals over the long term by feeding the BETO research-and-development (R&D) pipeline with fresh innovation. Within this framework, projects are further divided into core technology areas, enabling capabilities, and crosscutting support. The core technology areas house specific research programs directed at a particular challenge in alternative carbon utilization, enabling consortia aggregate infrastructure and capabilities that are of broad interest to the individual core technology areas, and they provide support as needed to solve a wide variety of programs throughout the portfolio. Finally, crosscutting support includes the Chemical Catalysis for Bioenergy Consortium (ChemCatBio) leadership, offering management of all projects within the consortia, and the ChemCatBio Data Hub, which is aggregating computational data in support of catalyst design initiatives.

STRATEGY

The Catalytic Upgrading Technology Area has a clear focus on reducing MFSP for biofuels or CO_2-derived fuels using catalytic processes, and techno-economic analysis (TEA) is front and center throughout. Programmatically, the strategy for reducing MFSP for biofuels is to reduce CapEx and OpEx through the design and synthesis of better catalysts. Tandem development of technologies that valorize lignin and produce high-value coproducts further decreases production costs.

Utilization of alternative, oxygen-rich carbon sources—biomass or CO_2—for the production of fuels and chemicals is challenging. Success will require a diverse set of technologies that are able to accept a variety of feedstocks and produce a spectrum of high-value (chemicals) and high-volume (fuels) products. Collectively, the Catalytic Upgrading Technology Area provides comprehensive coverage to the topics of relevance in alternative carbon utilization. Although the research needs in each program are unique and specific to that program, all of the efforts and technical targets therein contribute directly toward the programmatic goals of reducing MFSP to $3/GGE. This is appropriate considering the upcoming BETO go/no-go verification, which targets the production of biofuels at $3/GGE by 2022.

Engagement with industry and stakeholders is one of the strongest aspects of the Catalytic Upgrading Technology Area. Research directions are guided by input from a diverse, 10-member industry advisory board (IAB), with representatives from the energy, transportation, and commercial materials sectors. The IAB has been active in steering the portfolio in productive directions. Further, the program managers and project leaders have been responsive to prior input from peer reviewers. For example, peer reviewers in 2019 commented that an increased focus on high-value coproducts may be appropriate, and recent directions aimed at C4 products, such as BDO and high-octane gasoline additives, are responsive to this. In addition, 2019 reviewers highlighted the strength of DFA projects and the potential benefits of having them leverage enabling consortia. It was, therefore, appropriate to see an expanded set of DFA opportunities in the 2021 Peer Review and increased connections among DFA programs, the Advanced Catalyst Synthesis and Characterization (ACSC), and the Consortium for Computational Physics and Chemistry (CCPC).

Within individual projects, examples of engagement with industry and stakeholders abound. By their nature, all DFA projects directly engage industry in defining research directions, but this is not the only example. Within the AOP portfolio, there is overarching IAB input, and one can point to specific connections between industry and AOP projects. The CCPC, for example, is engaging with CanmetENERGY to model industrial biomass combustion facilities, which speaks to the direct applicability of the multiscale modeling efforts therein. In addition, efforts toward standardizing the characterization of feedstocks and pyrolysis oils through the development of ASTM methods have resulted from continuous engagement with commercial partners and stakeholders working in the area of fast pyrolysis.

It is also worth highlighting some particularly impressive connections with stakeholders in the FOA projects. The chemical-looping gasifier project at The Ohio State University (OSU) is working with Nexant, Shell Global Solutions, the Commercial Aviation Alternative Fuels Initiative, AdvancedBio, Kurtz Brothers, and Peloton. Further, the team at North Carolina State University (NCSU) is working with the National Renewable Energy Laboratory (NREL) and multiple paper mills to provide avenues for the valorization of paper-waste sludge. Their direct interaction with paper mills provides critical knowledge surrounding the demands of their target industry as well as the feed specifications that they should anticipate in working with real paper waste as a feedstock. Finally, the biogas upgrading project (University of South Florida, USF) is engaging directly with multiple regional biogas producers, again providing critical input from potential off-takers and guiding the development of the technology. Overall, the research directions and the evolution of the Catalytic Upgrading Technology Area represent clear, constant communication with IABs and stakeholders.

There are no clear gaps in technology or methodology in this program. The Catalytic Upgrading Technology Area gives comprehensive coverage to the various, broad technologies that comprise upgrading CO_2 or biogenic carbon, and all efforts are appropriately aimed toward reducing MFSP for biogenic fuels.

The Catalytic Upgrading Technology Area is making appropriate use of available funding mechanisms. AOP projects comprise most of the catalytic upgrading portfolio, which allows the program to capitalize on infrastructure and, importantly, orient the large team of well-trained scientists at DOE national laboratories toward their goals of reducing MFSP for alternative fuels. No doubt, the long-term support enabled through the AOP mechanism underlies the steady, continuous progress displayed in core research areas throughout the technology area. Along these lines, the continuous support provided through the AOP mechanism has produced world-class capabilities in enabling consortia, such as the ACSC, the CCPC, and the Catalyst Deactivation Mitigation for Biomass Conversion (CDM) programs. It is difficult to imagine funding these expansive and far-reaching consortia outside of the AOP framework. These crucial programs support nearly every core technology area, and the vast majority of foundational science in catalysis and reaction engineering comes from these programs. Similarly, the ChemCatBio Data Hub is a unique resource that provides large-scale access to computational data from diverse sources—this type of meta-project is really only possible through the stable, continued support offered within the AOP framework.

DFA projects are unique in that they forge partnerships between industry and national labs in order to solve problems that currently impede commercial deployment of biofuels and bio-based chemicals. These projects bring fundamental research capabilities, critical expertise in catalysis science, and the massive research infrastructure of national laboratories to bear on problems of current commercial interest. It is hard to imagine a better way to foster technology transfer and scale-up than engaging directly with companies trying to bridge to pilot and demonstration scales; as such, DFA projects are an excellent fit for BETO and the greater Office of Energy Efficiency and Renewable Energy (EERE) portfolio. As an example, in the CO_2 upgrading project (Opus 12), clear technological challenges are identified that prevent near-term commercial deployment of the electrolyzer stacks: high metal costs due to large particle sizes and failures in the electrolyzer membranes. By partnering with NREL, Opus 12 was able to leverage advanced synthesis and characterization capabilities (via ACSC) to reduce particle sizes and develop a facile, spectroscopic method for detecting failures in electrolyzer membranes.

FOA projects also provide an important perspective in the BETO catalytic upgrading portfolio. Specifically, they frequently engage academic institutions, which are well positioned for basic science and bench-scale exploratory work. In this sense, FOA projects are an excellent way for BETO to include relatively high-risk, lower-TRL projects in their portfolio. In the interest of the long-term, sustained development of bio-based technologies, it is crucial to continuously introduce new technologies to the development pipeline, and, in many cases, FOA projects are serving this purpose. For example, the team at the University of Tennessee working on a valerolactone-centered fractionation strategy has developed new technologies to convert lignin into high-quality, very high-value materials, such as supercapacitor-grade carbon. Preliminary analysis suggests that these types of lignin-based coproducts may be able to reduce MFSP for alkene-based biofuels to below $3/GGE. Considering that lignin valorization is a perpetual challenge for biomass refining, this is potentially a substantial impact. Alternatively, the biogas upgrading project at USF proposes an innovative, bifunctional core-shell catalyst to facilitate methane reforming and Fischer-Tropsch synthesis (FTS) within a single pellet, offering considerable intensification compared to a classic reforming/Fischer-Tropsch technology. Although it is early stage and relatively high risk, it has considerable potential for impact; thus, it represents an important component of BETO funding and the catalytic upgrading portfolio.

STRATEGY IMPLEMENTATION AND PROGRESS

Everything in this technology area is making clear contributions toward the programmatic goal of reducing MFSP for alternative fuels below $3/GGE by 2022. Individual technologies are diverse, but this is appropriate because there are innumerable challenges facing the production of biogenic fuels. Ultimately, successful biorefineries will need to draw from a robust and comprehensive technology portfolio. The Catalytic Upgrading Technology Area seems mindful of this, and they have constructed and continue to develop their research programs accordingly.

It is hard to identify a single project that is more relevant toward this goal because all are making outstanding contributions; however, we highlight contributions of the ACSC, the C1 team, the CDM program, and the CUBI program. Regardless of the specific technology, the ACSC team is always at the core of the design-development cycle. Their work continues to provide foundational knowledge of structure-property relations, and their approaches are, in many ways, leading the field in catalyst design. Impressively, they leverage a basic understanding of catalysis science to facilitate the design of next-generation materials, and their impact within the technology area cannot be understated.

Catalyst deactivation is a grand challenge throughout heterogeneous catalysis. The problem is particularly acute in biomass upgrading, where one must contend with high water content, high oxygen content, and impurities. The former is detrimental to the stability of the crystalline materials typically favored in oil refining (i.e., zeolites), and the latter can contribute both to surface oxidation and to coke formation. Lack of durability generally results in larger catalyst loadings, increased regeneration frequency, and, potentially, a shorter time between turnarounds. All of this increases operational cost and complexity as well as the capital investment required for a technology. For this reason, catalyst durability is a critical factor in determining the MFSP, so it is important that we understand catalyst deactivation and either develop new, more robust materials or envision better regeneration protocols. This is a major challenge in process integration, where one must contend with impurity carryover, and it is becoming increasingly important to address this aspect of catalyst durability as we move ever closer to pilot- and demonstration-scale facilities. Unfortunately, there is a critical knowledge gap in our understanding of catalyst stability, particularly when processing biogenic carbon. In this respect, the CDM program plays a crucial role in facilitating the next stage in commercial development. Given the scope of this challenge, and the ubiquity of catalyst deactivation in biomass refining, it may be worth considering further expansion of the CDM program through the allocation of additional resources.

The C1 program is noteworthy because it is providing a strategy for converting syngas directly to branched alkanes. This differs from conventional oligomerization-based strategies, which tend to produce aromatic-rich blends in the gasoline range. The selectivity to triptane achieved in this system is remarkable, and it represents an important development because high-octane gasoline additives may command a premium compared to base gasoline blends; as such, this program is likely in a good position to provide a near-term path to market via the production of high-octane gasoline additives.

Finally, the CUBI program is making important contributions in this area. CUBI is a large project that covers nearly every aspect of biomass upgrading that does not involve thermochemical processes (gasification, pyrolysis), so the research herein is broad; however, they are a critical component of the program because they are the only group in the AOP portfolio that is pursuing fractionation-based technologies. This is important because fractionation-based approaches allow one to isolate sugar monomers and lignin; as such, they allow for selective upgrading to specific molecules. For this reason, fractionation is the preferred starting point for the production of fine and specialty chemicals. Although fractionation-based methods are generally more expensive than those that use thermal methods to deconstruct biomass (e.g., pyrolysis, gasification), they offer opportunities for selective products, which can often be sold at a higher price than blends such as pyrolysis oils or fuels obtained by hydrotreating pyrolysis oils.

The Catalytic Upgrading Technology Area may well represent the leading edge of research in biomass upgrading. There are numerous examples of impactful projects, but it is also worth commenting that the program has an excellent management structure and portfolio scope, and, in many cases, they are establishing what should be considered best practices for research in biomass upgrading.

From within the AOP portfolio, the ACSC offers world-class capabilities in design, synthesis, and characterization, and they are unique in that they are enabling applied research goals through fundamental research into material properties and by advancing catalysis science at a very basic level. Although the CFP project is shifting scope to focus on refinery blendstocks, it is worth acknowledging that this team has set the state of technology (SOT) for pyrolysis research for the past 5 years, and they have developed what most consider to be the benchmark system for upgrading pyrolysis oils—platinum (Pt)/titanium dioxide (TiO_2), external fixed bed. The CCPC is doing outstanding work across the board, but one particularly impressive area is their advancement of the reaction engineering discipline through modeling and multiscale simulations. It is noteworthy that they have leveraged this skill set to anticipate the performance of full-scale reactors used for biomass combustion. The ChemCatBio Data Hub is constructing important cyber infrastructures for catalyst discovery. The effort to streamline inputs and allow for diverse data origins through user uploads is commendable. This should go a long way toward the data-driven design of catalysts and processes. The Thermochemical Platform Analysis provides crosscutting support in TEA and life cycle assessment (LCA), a critical component of new technology development. The methodologies and techniques that they have developed embody current best practices in TEA, so they are likely the standard bearers in this area. The CUBI program has made strides toward developing a BDO platform. This is a relatively novel direction for fractionation-based upgrading approaches. The BDO itself is produced through a metabolic pathway and may have considerable value as an industrial solvent; in addition, if it can be produced at appropriate cost and volume, it is an interesting platform chemical that could be used for the downstream production of fuels and chemicals that offer different properties from those derived from existing bio-based platforms—ethanol, hydroxymethylfurfural (HMF), and levulinic acid. Finally, the DFA project with Opus 12 is poised to enable direct conversion of waste CO_2 (e.g., fermentation, combustion off-gas) into fuels and chemicals using electrochemical methods, which are becoming increasingly attractive with the availability of green electricity. This collaboration has resulted in the development of viable electrolyzer stacks that are able to convert CO_2 into a spectrum of products.

The technology area is well positioned considering both near-/mid-term programmatic targets and the long-term needs of the field. With respect to the near-term goal of achieving an MFSP of \$3/GGE by 2022, several technologies are showing great potential. In particular, the C2 upgrading platform at Pacific Northwest National Laboratory (PNNL) can deliver ethanol-based distillate fuels at \$4.06/GGE without coproduct credits. They have mapped a strategy for reducing that number by an additional \$0.48, and they can include n-butene as a coproduct, resulting in a final MFSP of \$3.16, which is very close to the 2022 target. Further, their technology clearly produces a viable aviation fuel, as demonstrated by LanzaTech, which licensed this technology and partnered with Virgin Airlines for a demonstration flight on bio-based jet fuel in 2018.

A parallel C2 upgrading project at Oak Ridge National Laboratory (ORNL) has also been successful. They have reduced ethanol upgrading costs from \$1.35/GGE to \$0.60/GGE using a zeolite-based technology. Impressively, the platform has already been licensed by Prometheus and Vertimass to produce distillate/jet fuels. It is also worth noting that the ORNL process enables the flexible coproduction of butadiene—specifically, the team has demonstrated tunable selectivity through relatively straightforward manipulation of hydrogen (H_2) partial pressure in the reactor. Butadiene is an intriguing coproduct, considering that its supply has been somewhat constrained by the recent decline in naphtha cracking. It is a relatively high-value product compared to distillate fuels, so the ability to produce it in targeted quantities through the manipulation of operating conditions is attractive. Finally, with a three-step dimethyl ether (DME) to high-octane gasoline process, the C1 program was able to attain an MFSP of \$3.53/GGE, with the potential to improve further as 2022 approaches and they bring a direct syngas-high-octane-gasoline technology online. Even if they see further improvement from their current \$3.53 benchmark, it is worth pointing out that they are selectively producing triptane, which is a higher-value additive than a conventional gasoline, so \$3.53/GGE is already an attractive MFSP for this product.

The portfolio also includes some lower-TRL work, which is less likely to meet a \$3/GGE target in 2022; however, these new directions are leading to the discovery of new platform chemicals and new families of fuel and/or chemical products that are potentially accessible from biomass. Much of the work in the CUBI portfolio falls into this category. For example, they are now producing 2,3-BDO using fermentation. BDO may have considerable value as a solvent or chemical commodity. Alternatively, it is a polyfunctional intermediate that opens the door to downstream chemistries that have not been accessible through upgrading the conventional suite of bio-based platform chemicals.

As a final note, this technology area supports innovative work in catalyst design, such as the biogas upgrading project housed at USF. This program is developing an entirely new class of materials designed to couple reforming and Fischer-Tropsch in a single pellet. If successful, they could considerably reduce the footprint and CapEx typically associated with synfuels. Further, they are positioning themselves to convert biogas—comprising two greenhouse gases (CO_2 and methane [CH_4]) into liquid fuels, which is preferable to the direct methane emission that is often associated with unutilized biogas.

At the project level, management is generally well defined, and projects adhere to their stated goals. Management for this program really shines, however, in the enabling technology consortia (ACSC, CDM, CCPC) and crosscutting support areas (ChemCatBio, Data Hub). These are large initiatives, and the leadership must manage projects or portions of projects across the entire technology area. Although the AOP supports a diverse set of research projects, everything within is tightly integrated, and all projects are in joint pursuit of a single goal. As an example, TEA work is housed primarily within the Thermochemical Analysis Project, but this group connects with and guides research for nearly every project within the technology area. Similarly, the CCPC, CDM, and ACSC performers have strong ties to every program that they support. Overall, each performer presented a clear, coherent, and consistent research program, and everyone is tracking closely to real-world deliverables despite the size of the program and the foundational knowledge they are generating along the way. All of this requires excellent management, constant communication, and coordination between the individual project managers, the managers of supporting consortia, and the technology area leadership. Overall, the Catalytic Upgrading Technology Area sets a great example for how to properly manage large research programs.

RECOMMENDATIONS

First, high-value chemicals and materials have the clearest near-term path to market; accordingly, the program is encouraged to increase its focus on ancillary technologies for producing high-value chemicals alongside core technologies that focus on producing high-volume fuels. Second, catalyst stability remains problematic across the entire portfolio, and challenges presented by deactivation are likely to increase as technologies continue to mature and move toward process integration. Expanded access to ACSC and CCPC capabilities during the past decade has benefitted the entire portfolio. Along these lines, it would be prudent to expand the scope of the Catalyst Deactivation Mitigation program such that they can more effectively support efforts in process integration. Third, eventual full-scale deployment of these catalytic technologies will require a transition to relatively large and formed catalyst pellets as opposed to the powders more common to bench-scale research. Mindful of this, the program is encouraged to develop strategic partnerships with catalyst manufacturers to begin the process of scaling up next-generation materials.

CATALYTIC UPGRADING PROGRAMMATIC RESPONSE

INTRODUCTION

The Conversion R&D Program would like to thank the five Catalytic Upgrading session reviewers for their time and careful review of the projects presented in this session. We recognize that this was a challenging review process within the context of the multiple virtual concurrent sessions, making it difficult to see the broad reach of the entire Conversion R&D Program.

BETO appreciates the Review Panel's recognition of the successes of consortium-based research, acceleration of the catalyst design cycle, and systematic reduction of modeled MFSP estimates through catalyst performance improvements, process intensification, and production of high-value coproducts. Additionally, the Review Panel recognized the critical importance in leveraging the unique strengths of the consortia while funding industry partners in moving technologies toward commercialization. The Review Panel noted that there were no specific gaps in technology or methodology within the technology area, and it is making appropriate use of available funding mechanisms. BETO is especially appreciative that the panel noted that the long-term support of the DOE national labs and ChemCatBio has produced world-class capabilities in enabling activities, and these programs have had far-reaching results. In particular, the DFA projects have linked industry partners with the enabling programs to address barriers to commercialization, thus demonstrating real market impact. Similarly, BETO will continue to focus on real-world challenges within catalysis by leveraging high-performance computing to model catalysts and reactors while targeting process integration and intensification with a focus on de-risking technologies for future development efforts. BETO intends to continue to support industry partners by leveraging national lab capabilities through the various consortium national laboratory-led projects, DFAs, and competitive funding opportunities.

The Review Panel stated that as the specific technology pathways within the technology area continue to mature, process integration and systems integration will be a critical focus area. The Conversion R&D Program agrees and will continue to pursue R&D that further de-risks these technologies to sufficiently move up the TRL scales where industry can support further development and commercialization efforts. Although the Review Panel identified some technologies that have potential to go on to pilot scale-up activities, note that these efforts are largely funded by the Systems Development and Integration program, which cannot fund all technologies and pathways without industry support.

Recommendation 1: High-value chemicals and materials have the clearest near-term path to market; accordingly, the program is encouraged to increase its focus on ancillary technologies for producing high-value chemicals alongside core technologies that focus on producing high-volume fuels.

BETO acknowledges the importance of high-value coproducts that can enable biofuel production. TEA work continues to show the importance of leveraging high-value chemical production alongside fuels, and these analyses are being utilized to guide experimental R&D efforts because many of these approaches are still at an early- to mid-stage development, with additional de-risking R&D necessary to achieve commercialization goals. TEA methodology will continue to focus on both separately and combined technology related to fuels and coproducts while making clear the assumptions and associated risks. This work has allowed for increased understanding of how specific coproduct technologies can be integrated into various systems, improving commercialization potential for fuel production. Although the majority of projects reviewed within this session are focused on hydrocarbon production, the Performance Advantaged Bioproducts Consortium is in its third year of activities and has the stated mission of exploiting biomass properties for higher-value chemicals that could support near-term commercialization efforts; unfortunately, the reviewers were not able to attend these sessions due to the concurrent scheduling.

Recommendation 2: Catalyst stability remains problematic across the entire portfolio, and challenges presented by deactivation are likely to increase as technologies continue to mature and move toward process integration. Expanded access to ACSC and CCPC capabilities during the past decade has benefitted the entire portfolio. Along these lines, it would be prudent to expand the scope of the Catalyst Deactivation Mitigation program such that they can more effectively support efforts in process integration.

BETO recognizes the critical importance of catalyst deactivation and mitigation approaches; the CDM project has made considerable progress in its first 2 years. BETO’s support of this project has resulted in the development of a broader understanding of deactivation pathways related to core technology pathways within ChemCatBio that could be applied to new catalyst materials and properties as they are developed. Additionally, the results of CDM’s work have emphasized what the Review Panel has mentioned regarding the importance of understanding deactivation pathways as they relate to process integration. Already, this project’s findings have led to new analytical and characterization techniques that have informed mitigation strategies related to catalyst regeneration and other potential deactivation pathways. BETO recognizes that any projects involving catalytic research must include deactivation and mitigation components that are tailored to the individual technologies and will continue to require milestones that target these areas. Additionally, BETO will continue to leverage learnings from ChemCatBio for the best practices of incorporating R&D that include catalyst deactivation and mitigation approaches for future funding opportunities.

Recommendation 3: Eventual full-scale deployment of these catalytic technologies will require a transition to relatively large and formed catalyst pellets as opposed to the powders more common to bench-scale research. Mindful of this, the program is encouraged to develop strategic partnerships with catalyst manufacturers to begin the process of scaling up next-generation materials.

BETO acknowledges the challenges catalyst manufacturers face in terms of the design and synthesis of novel catalysts. An additional hurdle is that existing catalysts may also contain cost-prohibitive materials. The Systems Development and Integration Program supports the Engineering of Catalyst Scale-Up project (WBS 3.3.2.701/702), which facilitates the transition from lab-scale catalyst formulations (powdered catalysts, colloidal nanoparticles, etc.) to extrudates and pellets that are crucial to industrial scales and demonstration efforts. This project also leverages a diverse industry board to guide scale-up efforts and maintain relevant targets, methodologies, and performance metrics. Further, BETO’s Catalytic Upgrading Technology Area supports this work through robust computational modeling and validation efforts that can predict reaction mechanisms, deactivation, and performance under different operating conditions. R&D results from this work have also been leveraged in the CFP project, which utilized engineered catalysts in recent experimental tests that have validated several important performance assumptions related to product yield, catalyst lifetime, and regeneration. Further, members of ChemCatBio are always looking for partnership opportunities with industry.

THERMOCHEMICAL PLATFORM ANALYSIS

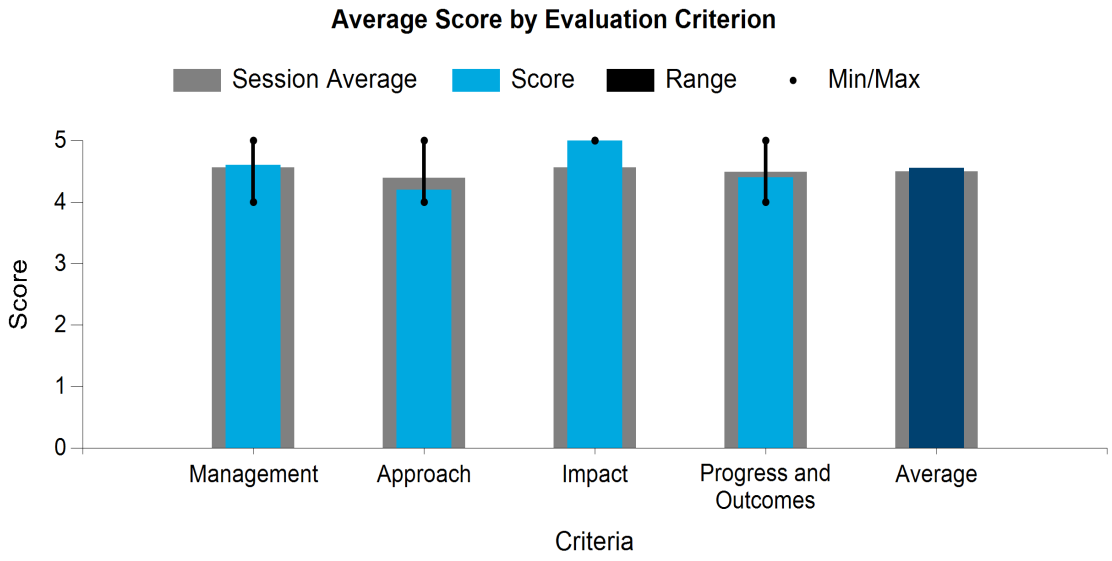
National Renewable Energy Laboratory

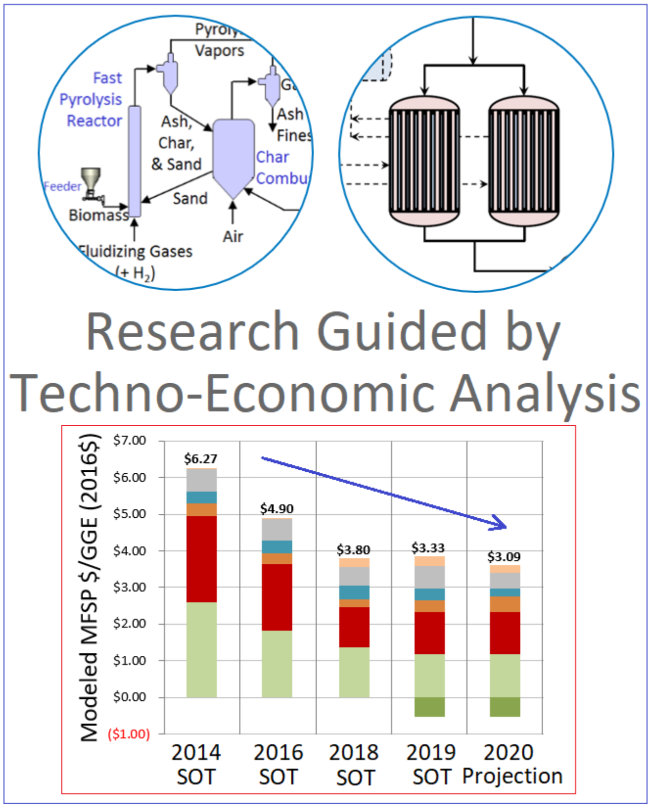
PROJECT DESCRIPTION

WBS:	2.1.0.302
Presenter(s):	Abhijit Dutta; Adam Bratis; Zia Abdullah
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2022
Total DOE Funding:	$1,400,000

The objective of the NREL Thermochemical Platform Analysis project is to inform and guide R&D priorities for thermal and catalytic conversion processes by providing process design and TEA. This is achieved through close collaboration with researchers and external experts, along with both the use of commercially available modeling tools and the development or use of collaboration-derived, domain-specific tools and resources, such as refinery integration, kinetic and reactor models, phase equilibrium models, and pertinent bioproducts market studies.

This project is directly aligned with BETO’s goals, with enabling technology advancements and cost reduction for biomass-derived biofuels being one of its primary objectives. TEA-guided research facilitated by this project has helped achieve significant modeled cost reductions for the *ex situ* CFP pathway and the indirect liquefaction (IDL) pathway for the conversion of syngas to high-octane gasoline. Cost reduction through refinery integration, development of valuable coproducts, and other options are being identified for future research to help reduce the modeled MFSP to $2.50/GGE by 2030. Additional priorities anticipated in the future, such as the use of renewable electricity for liquid fuels and products and emphasis on waste utilization, are also being explored in conjunction with research on the catalytic utilization of syngas and other gases (including CO_2). Industry-relevant parameters are given deliberate attention as part of the work done under this project to help answer questions important for future commercialization and address associated risks.





Research Guided by Techno-Economic Analysis

Photo courtesy of NREL

COMMENTS

- Dutta's work on TEA may be the most widely read of all the BETO (even DOE!) publications. As a consultant for numerous companies, from startups to mature international behemoths, I find that most of our clients are keenly interested in TEA. So, this work is very useful for us. No one ever believes the economic results presented by companies because they have an interest in showing their processes in the best light. But NREL work provides a "neutral" view. And the detail in your studies can, and does, often form the basis for our own TEA. Your focus on the topics of pyrolysis, catalytic pyrolysis, and syngas upgrading are timely. And your transition to refinery coprocessing is another area of keen and growing interest. The only criticisms I have heard are about some of the assumptions made in the studies.

- The management is well organized considering the complexity of the multiple interactions and feedback needed to progress the models. This was another key area with appropriate funding. I'm happy to see the collaboration with ExxonMobil, which indicates the relevance of their work results. I have always viewed this team as efficient and very productive considering the high challenge for them based on variables being input to them to manage and refine their calculations. A key question for the management is how to get more engagement with broader oil and gas suppliers because their models are quite valuable and feedback from industry will always provide improvements. I see no outages or gaps in the modeling work. Modeling is key to progress toward pilot and scale-up programs where the investment and risks becomes quite high. I'm happy to see modeling is now a way to define continuation or the wrap-up of approaches as well as shifting focus due to modeling. The progress and outcome for the programs shown toward economics of $3/GGE is clear, and, as shown, some are within the range of the GGE goal with thermochemical, but scale-up will present unforeseen issues, which modeling may not predict.

- The goals of the Thermochemical Platform Analysis project are very clear, as indicated on the quad chart on slide 29, to inform and guide R&D priorities for CFP, high-octane gasoline, and IDL pathways using TEA and LCA. Key process metrics (e.g., MFSP) and key performance indicators (KPIs) were provided on slides 37–45 for CFP and high-octane gasoline, along with projected process performances. Additional project metrics could also include how many key decisions have been altered due to Thermochemical Platform Analysis information and the cost savings or cost/time avoidance as a result. Other high-level goals mentioned include process simulations at larger scales and quantifying the impact of new research results on process models as well as suggesting alternative pathways. All of these goals have immense value for R&D. The project team is highly collaborative and productive, as indicated on slide 19, with input from NREL, Idaho National Laboratory (INL), Argonne National Laboratory (ANL), and PNNL. The priorities of the work queue and roles of the team members were not as apparent. Key notable overall project risks provided on slide 12 include alternate R&D approaches, rigor, and prediction capability. These risks are mitigated by setting priorities, making the right partnerships, and having alternative models ready to launch. CFP risks were identified on slide 18 as carbon balance closure mitigated by acetone and methyl ethyl ketone (MEK) adsorption-based recovery, along with refinery co-hydrotreating steps. No risks were identified for the high-octane gasoline and IDL pathways as of now. The key end-of-project milestones and targets were provided on the quad chart—namely, identification and quantitation for all CFP pathways and products that can be integrated within a traditional refinery environment. The communication plan was not explicitly stated because it is built into the workflow. It is clear that frequent interactions are happening, as presented on slides 8 and 19. The organization and coordination of these interactions needed further explanation, in particular the industry advisors and subcontractors. The current SOT of the TEA and LCA based on process simulation has a standard principle surrounding the approach. Here, the standard tools—e.g., Aspen, Excel, and Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies (GREET)—are implemented, so there is no SOT advancement per se. The quality of the estimates is based on the accuracy of the data used in the models. The new approach for coprocessing is an exciting new direction. The linear programming work provided by ANL using Aspen PIMS should be used in tandem with this effort so that the impact is not too unit-specific. Most of this effort is rooted in good solid approaches for process modeling and supports the BETO Conversion R&D 2022 goal to deliver feedstocks and complete verification operations at the pilot scale for an alternate conversion pathway with fuel production cost modeled at $3/GGE for 2,000 tons of feedstock/day. The Enabling Technologies area under the Chemical Conversions to Intermediates and Products direction is supported by developing new analytical and modeling tools that enable more efficient production of fuels and products across conversion. The work is necessary and essential for BETO’s success. The current approach may not move the innovation needle. The current approach will enable key R&D decisions to be made and mitigate significant risks along the way, which may be more critical for ChemCatBio. The team was able to clearly show that project work directly connects and impacts the 2022 go/no-go verification decision for the conceptual CFP process design proposal at the front-end loading (FEL)-1 level, enabling this work to move into the next engineering design workflow with an external engineering, procurement, and construction (EPC) vendor. Further, there is broad impact of this work in setting the process simulation SOT and allowing models to be published and available. Publications are widely read across the community. The opportunity to license detailed models, as well as patents, including experimental and modeling work, was briefly mentioned on slide 17. The team is currently working with ExxonMobil on biomass pyrolysis projects, which could lead directly to commercial applications, especially if the go decision is reached in 2022 and an EPC is selected to take things to the next level. There was some notable progress toward the project goal of informing and guiding R&D priorities for CFP, high-octane gasoline, and IDL pathways using TEA and LCA. For CFP, the stand-alone hydrotreating conceptual process design was complete. More comments regarding the steps and cost of coproduct cleanup should be given, as well as the total organic carbon expected in key wastewater streams. The plan is to use a thermal oxidizer to deal with the wastewater, and swing adsorption was the plan for the coproduct cleanup. The risks that still exist preventing stand-alone scale-up must be clearly listed and published because this was critical information for changing the R&D priority to coprocessing. A current draft of the syngas-to-high-octane gasoline conceptual block flow process design includes all commercial areas except for the high-octane gasoline section, which should help improve FEL-0 estimates. The team was able to provide an SOT direction to the high-octane gasoline team, suggesting priorities to be focused on using real feeds, integrated runs, increased yields, regeneration, and design of experiments for catalyst formulation. An alternate pathway for single-step DME conversion was suggested with a focus on optimizing the catalyst and conditions for reducing the production of C4 and CO_2. The recommendations on R&D priority should be clearly listed in a separate table to support these results. Some progress has been made in identifying and quantifying all CFP pathways and products that can be integrated within a traditional refinery environment with the completion of the stand-alone case. No preliminary work was presented yet on the coprocessing case.

- The Thermochemical Platform Analysis project provides TEA for the other projects. This is a unique role in the whole program, especially because the focus of the program is on applied technologies to promote bioenergy. The team performs its role very excellently. Bioenergy may face a rapid change market eventually. It could be beneficial if the TEA can be done considering the variation of price and needs of the market. Indeed, this may be a stretch, and there are many aspects beyond technologies. It would also be interesting if the TEA can integrate with the other computation effort to form a “virtual” design platform aiming to combine the design of catalysts from the atom level to process.

- This team provides enabling support to nearly every program in the catalytic upgrading umbrella. This is important because TEA helps to identify risks and technical areas that are most in need of additional effort. In this sense, TEA directly serves to de-risk technology transfer and commercial development of biogenic fuels and products. Overall, this team has set best practices for using TEA as a tool for guiding applied research in the biomass upgrading space. The team is encouraged to continue using TEA in a relative sense to focus research effort on primary cost drivers and to de-emphasize absolute dollar-per-GGE targets to the extent possible.

  Management: There is a clear channel of communication between core TEA team and research areas in need of TEA. The team also has open channels with external suppliers, computational researchers, National Institute of Standards and Technology (NIST) databases, feedstock consortia, and LCA teams, ensuring robust TEA. Risk identification, risk management, communication, and advisory board interactions are all built into workflow. Overall, the project is extremely well managed. Subcontracts are helping to scale up pyrolysis and predict fuel properties, but it is unclear how subcontractors are expanding the tools available to this consortium already.

  Approach: The technical tool kit available to this team spans everything from quick assessments of new processes to rigorous analysis of more mature concepts. They use appropriate tools for TEA—these include Aspen, Excel, and GREET—all of which comprise modern standards in this type of research. I liked the use of sensitivity analysis and Monte Carlo methods to address limited data or uncertainty in available data. The connection with feedstock consortia can provide better input as to raw material prices. This is important because raw materials are one of the major cost drivers in a biorefinery. Overall, the project is delivering process models with some predictive capability, which helps to de-risk future scale-up. There have been changes in the project portfolio. In the CFP program, the team is shifting from stand-alone hydrotreating to refinery coprocessing and assessing the impact of using low-cost/low-quality municipal solid waste as a feedstock. The team has taken on new projects in syngas upgrading optimization, considering recycle, process intensification, and diversified feedstocks (solid waste/CO_2). All of these are generally appropriate directions, though it is worth noting that considerable scientific progress has been made in the CFP program, and additional research in the area is worthwhile even if it cannot meet 2022 verification targets. I understand the programmatic focus on using TEA to estimate MFSP relative to absolute targets, but it may be preferred to use TEA in a relative sense to identify primary cost drivers and direct future research.

Impact: TEA is helping to accelerate the adoption of biogenic fuels and products by de-risking early-stage technologies. Collaborations with industry are positive, and this team has shown that research within this consortium continues to reduce MFSP and show improvement in the SOT. The team is disseminating knowledge through publications, and they have made sample models and tools publicly available, which is outstanding. I was particularly impressed that TEA identified a risk in lack of carbon balance closure during CFP with stand-alone hydrotreating. This directed research toward analytical methods to close the carbon balance. Ultimately, this increased the MFSP and led to a pivot away from stand-alone hydrotreating, but the impact is huge given the extant challenge in pyrolysis oil analysis and the errors propagating throughout the field due to inadequate quantitative analytics.

Progress: The team has provided a detailed TEA for CFP with stand-alone hydrotreating. Research showed a clear reduction in MFSP and identified key risks.

PI RESPONSE TO REVIEWER COMMENTS

- Thank you for your valuable comments and feedback. As recommended, we will continue to engage with the petroleum industry. As part of 2021 efforts for the CFP pathway, we plan to publish our recent learnings; this will include the impacts of experimental results from co-hydrotreating of CFP oil and the recovery and purification of light oxygenates from CFP. The percentage of biomass carbon lost in aqueous streams will continue to be listed as a metric in the SOT table; this metric usually correlates with the percentage of oxygen in CFP oil. Projected cost advantages guided our decision to investigate co-hydrotreating versus stand-alone hydrotreating of CFP oil; our learnings from successful single-stage stand-alone hydrotreating helped guide our researchers in this regard. Additional refinery coprocessing-related work will be published as we make progress. We do have TEA-guided decision points for the IDL-to high-octane-gasoline pathway, with additional analysis planned for a go/no-go decision in Fiscal Year (FY) 2021. Subcontract work under our TEA project is usually of specialized nature, allowing deep dives outside our regular workflow to help answer relevant research and TEA questions. As illustrated in the presentation, we have interactions with the CCPC for detailed modeling, with our diverse workflows integrated using simplified correlations; we will continue this approach. We try to be transparent with our assumptions and understand that the industry usually works off different business models based on specific situations; we hope that the details provided in our studies allow the revision of our results using different sets of assumptions.

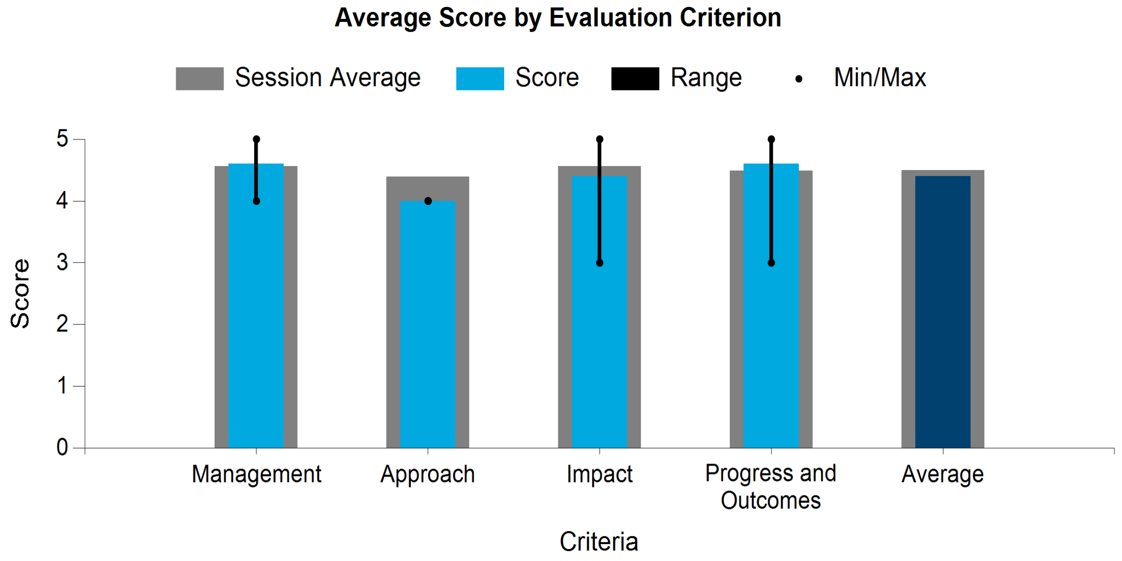
LIQUID FUELS VIA UPGRADING OF INDIRECT LIQUEFACTION INTERMEDIATES

Oak Ridge National Laboratory

PROJECT DESCRIPTION

WBS:	2.3.1.100
Presenter(s):	Jim Parks; Tim Theiss; Zhenglong Li; Missy Miller
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2022
Total DOE Funding:	$1,200,000

This project targets to develop efficient one-step ethanol to C3+ olefins (ETO) technology to enable high carbon efficiency to liquid hydrocarbon fuels at lower cost and enable the development of a market-responsive biorefinery concept through the C2 platform, providing control over gasoline, diesel, and jet fuel as well as high-value coproducts. The outcome is to advance C2 upgrading technology and reduce commercialization risk by addressing catalysis and process challenges and demonstrating liquid fuel production at a modeled MFSP of $3/GGE. Research tasks primarily include ETO catalyst and process development, coproduct development, and oligomerization reaction optimization. Multifunctional Lewis acid zeolite catalysts are developed to catalyze cascade ethanol conversion to selectively produce targeted butene-rich C3+ olefins (89% selectivity at ~100% ethanol conversion), which can be further upgraded to a high yield of middle distillates. The ETO catalyst structure-function relationship has been explored through the collaborations with ChemCatBio enabling projects. Such C2 upgrading technology helps to meet the needs of ethanol producers to diversify the product portfolios and address the decarbonatization challenges for heavy-duty transportation and aviation sectors.



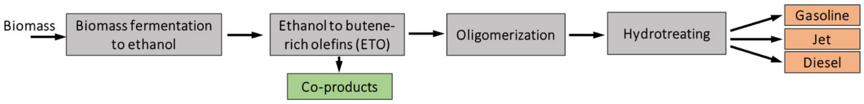


Photo courtesy of ORNL

COMMENTS

- As with all of these projects, use of TEA to guide the work is very important and is a very positive aspect of the whole program. The catalyst deactivation/regeneration experiments (slide 17) indicate to me that this process might be better operated in a fluid bed where catalyst regeneration is much easier. Understanding the active sites, and being able to selectively deactivate these, is a promising approach with good preliminary results. The mixed catalyst—CuZnY/beta Pt/Cu—shows great promise at avoiding butadiene formation. But is butadiene a more valuable byproduct? The science in this project is quite good, but I wonder if the project can be economically viable under reasonably imagined conditions.

- Excellent job organizing and utilizing external and internal technology development via licensing external and catalyst development internal. It is clear from the presentation that the challenge is using ethanol from biomass to meet economics. The defined approach is clear, as reducing the number of steps and minimizing energy input is the right approach. There are still issues with ethanol as a feedstock due to the current value and cost of ethanol from biomass. Explaining the potential upfront that other existing ethanol production could benefit from this process to get over the blend wall issue is a smart start. Key will be future cost reduction in biomass to ethanol to have the greatest impact and the volume potential of feedstocks because corn and sugarcane still require growing food-type crops, which needs to be challenged in the future. No issues are seen with the progress and outcome to date; the only concern is using ethanol from existing processes as the start point, with concern that future biomass to ethanol will not be viable as a feedstock at reasonable economics for fuel. There is some outstanding technology development in this program advancing the state-of-the-art (SOA) catalytic processes.

- This appears to be the ORNL side of the ETO technology C2 Upgrading project, which is even lower risk and quite successful with the Prometheus opportunity. The goal is to upgrade ethanol to middle distillates. The ethanol-to-jet (ETJ) route is the benchmark going through ethylene and olefins to jet-range hydrocarbons. The team is looking for opportunities to do this in a single step. Long-term catalyst durability and regeneration continue to be the challenge. There are several milestones associated with risk mitigation in FY 2021. The approach is to reduce the diffusion length of the olefins in pore confinement to hinder aromatization chemistry. This approach should advance the SOA of ETJ. The innovative portion of this strategy really focuses on the coproduct generation. The group is doing fundamental research that includes computational modeling. The team understands that this work could really change the processing flexibility for ethanol producers and also provide a clean source of distillate to the petroleum refining industry. Vertimass has already licensed technology developed from this project. Originally, the team looked at beta zeolites for including metal sites. They can make 90% C3 olefins at almost 100% conversion at 623 K. The collaboration with CCPC has identified opportunities to eliminate the dehydration reactions completely. The team was able to show excellent water tolerance as well as excellent selectivity control by varying the levels of hydrogen partial pressure. They also showed that they can produce enough H_2 *in situ* to help drive the entire reaction network.

- This project develops zeolite-based catalysts that produce fuels and valuable coproducts from ethanol. The team is developing a type of very interesting nanoporous catalysts. The nanoscale confinement could alter the electron distribution on the substrate and thus change the catalytic ability. The nanoscale confinement could also preselect the molecules that can approach the active sites and the conformation of the molecules. Such confinement effect could open gates to many opportunities. It could be beneficial if the team collaborates closely with the CCPC and investigates the mechanisms and designs catalysts based on the mechanisms. This project, aligning with the other projects, emphasizes the importance of valuable coproducts in the development of a biorefinery. The coproduct direction should be seriously considered.

- This project is exploring zeolite-based pathways for upgrading ethanol to distillate fuels, olefins, and butadiene. Overall, the work is solid, and there are no real weaknesses.

  Management: The conversion pathway is clearly outlined, as are the focus areas for this project. The team has clear connections with enabling consortia and complementary research programs at various national labs. The goals for this project are clearly defined. Risks are identified with appropriate mitigation strategies, and specific milestones are tied to risk mitigation. Overall, the management of this project is strong.

  Approach: Parallel to the C2 program, this team is working on an ethanol-to-distillates technology, which is appropriate due to the increasing availability of low-cost bioethanol and a blend wall in the gasoline sector. The team is using a cascade of dehydrogenation/condensation/hydrogenation/dehydration, so they need to design bi-/multifunctional catalysts to facilitate the multiple chemistries in an intensified process. They are aiming to maximize carbon efficiency to liquid hydrocarbons and understand deactivation while collaborating with appropriate programs to develop fundamental insights in parallel with their pursuit of applied goals. Pillared zeolites are a reasonable approach for mitigating deactivation and decreasing aromatic formation by making a non-shape-selective catalyst, but it was not entirely clear how this would be superior to perhaps a mesoporous solid acid. I recall that some of the existing olefin-to-distillates technologies avoid confined pores for this reason, so there may be appropriate technology already out there.

  Impact: A direct ethanol-to-distillates approach avoids the need for separate ethylene and olefin oligomerization strategies that might be typical in an ETJ-via-ethylene strategy. Note that a single-step ethanol to C3 olefins is attractive considering a potential supply gap in C3 olefins due to the decreasing naphtha cracking in the shale gas boom. There is considerable potential for impact here; ETJ technologies address the extant need for a better product portfolio for ethanol producers while also addressing a long-term need for liquid alkane aviation fuels. The collaboration with Prometheus is interesting because it is using CO_2 as an ethanol feedstock and converting it to butadiene and jet. If successful, this could be a nice carbon-negative fuels technology.

  Progress and outcomes: The team has made significant progress in understanding catalyst structure and performance through outstanding collaborations with ACSC and CCPC. The work highlights the significance of atomically dispersed metal sites, which is interesting. The effort to improve catalyst stability is significant, particularly in the presence of water because this can allow wet ethanol processing and reduce the separation burden required to move beyond the ethanol/water azeotrope. The team has developed insights into how operating conditions impact activity and selectivity, which is critical to allowing product flexibility and enabling switches between butadiene and olefins, depending on the intended product.

PI RESPONSE TO REVIEWER COMMENTS

- We appreciate the positive feedback on ORNL’s ethanol upgrading project. We also agree with the assessment on the catalyst durability challenge, which is one of the focuses as we continue to develop this technology. We appreciate the great comment on our technology development to advance the SOA. At the same time, we also understand that the ethanol feedback cost is one of the major contributions to the overall fuel production cost, which is generally the case for most of the biomass conversion technologies. There are challenges to produce middle distillate that can directly compete with petroleum-derived fuels in the current market situation. We believe the coproduct production is one of the strategies to meet this challenge, which reflects the advantage of our technology—flexibility to product fuels and chemical coproducts in one process. We appreciate the reviewer's positive comments on this work. The notes on the potential high demand of renewable C3+ olefins and using CO_2 as an ethanol feedback provide further good justification of the work. The C2 upgrading team has very close collaborations with CCPC on understanding the catalyst structure and reaction mechanisms. The findings from modeling will be used to guide our further catalyst design and development. We also agree on the coproduct value, which is one direction we will focus on. Catalyst deactivation and regeneration is ongoing work in FY 2021. We will incorporate what we learn further into the consideration of reactor choice when we start to plan for technology scale-up. The physical mixture of ZnY/Beta and Pt/copper (Cu) catalyst offers the flexibility to make either butene-rich olefins (for fuel or chemical production) or butadiene. This flexibility is very important for a technology that can meet a dynamic market demand.

CATALYTIC UPGRADING OF BIOCHEMICAL INTERMEDIATES

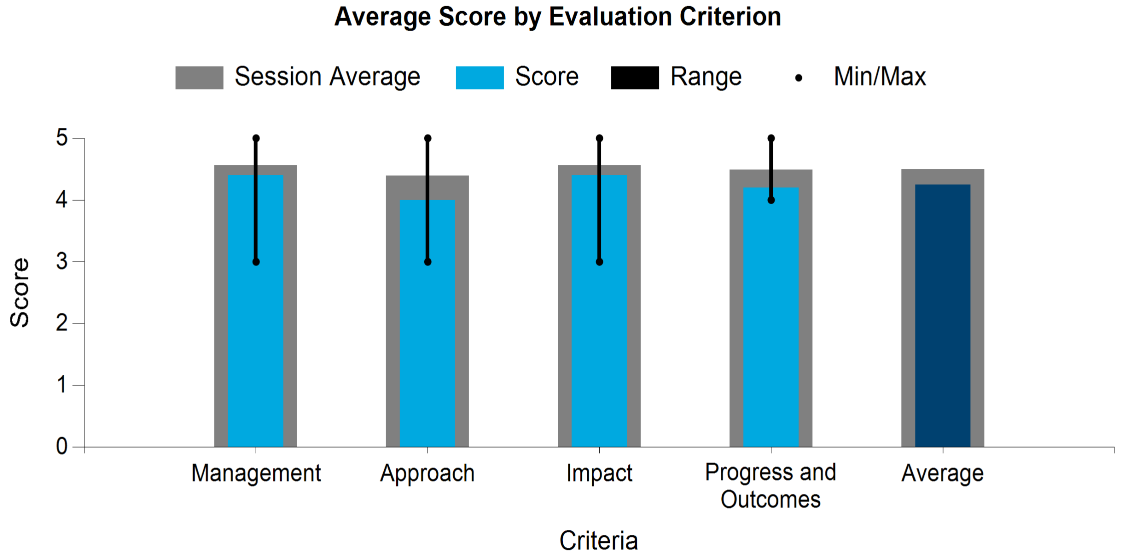
National Renewable Energy Laboratory, Oak Ridge National Laboratory, Los Alamos National Laboratory, and Pacific Northwest National Laboratory

PROJECT DESCRIPTION

WBS:	2.3.1.101
Presenter(s):	Adam Bratis; Richard Elander; Zia Abdullah
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2022
Total DOE Funding:	$6,250,000

The CUBI project is a multi-lab effort within ChemCatBio that is focused on improving the catalytic upgrading of intermediates from biochemical deconstruction and/or biological conversion (i.e., fermentation) to fuels and chemical coproducts. This is accomplished by developing catalysts with improved performance and durability, mitigating the impact of biogenically derived inhibitors (including water), and evaluating intensified processes to reduce separations requirements and improve carbon utilization. Specific catalytic upgrading routes being developed are (1) fermentation-derived 2,3-BDO, (2) fermentation-derived carboxylic acids, and (3) lignocellulosic sugar-derived furfurals. These routes represent key technology pathways being investigated within BETO's biochemical conversion portfolio.

By utilizing experimental and characterization capabilities and modeling tools across the four CUBI labs and collaborations with ChemCatBio-enabling projects, the CUBI project is advancing catalytic upgrading process performance and robustness. Its impact is already well established by several high-impact journal articles and patent publications, along with industry engagement in related, competitively awarded collaborations. The CUBI project will result in >25% MFSP cost reduction in the catalytic upgrading section of integrated biochemical conversion routes, as quantified by ongoing TEA modeling.



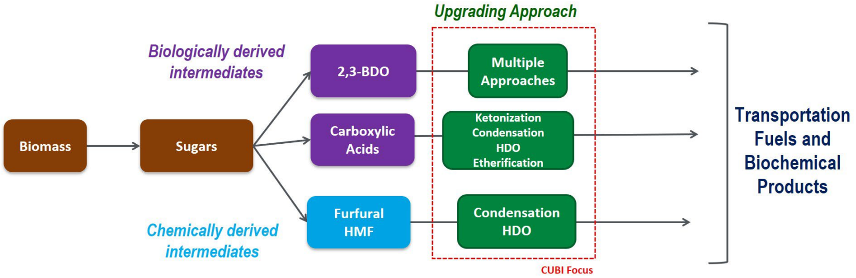


Photo courtesy of NREL, ORNL, Los Alamos National Laboratory (LANL), and PNNL

COMMENTS

- There is no issue with the management and organizational structure. Key aspects highlighted indicate strong collaboration across this complex program. There is excellent progress by the catalyst teams on a very challenging program; however, the true value to BETO may be to keep the biomass sugar-derived 2,3-BDO as a solvent for new uses, in my opinion, to reduce the final cost of other routes to fuel. Does the team or their partners have a benchmark assessment of impact/value of 2,3-BDO without further conversion? This was not presented. I have worked on many solvents over my career, including 2,3-BDO, and I believe it is a substantial upgrade over 1,2-propanediol and even the higher-value di-propylene glycol and tri-propylene glycol solvents. Currently, the only available bio-derived solvents for the consumer goods industry and other uses are glycerin and glycerin-derived 1,2-propanediol. Converting 2,3-BDO to butene, then upgrading, also seems to be counterintuitive because butene prices globally are in the range of $1.20/kg. The impact could be substantial for biomass-derived 2,3-BDO, in my opinion, keeping the material for chemical use. The current resulting GGE analysis of $8.62 does not justify the approach for fuel, and, as such, I am struggling to see the ability to reach the 2030 goal with further development to fuel. I also struggle with projections for 2030. There are too many factors affecting costs in the future that make this a challenge. I found the catalyst work on specifically butene very promising, which may be obtained by other routes than 2,3-BDO. Catalyst deactivation seems to be a grand challenge overall. Finally, has the team considered concentrating BDO by freeze fractionation? The material is crystalline below 3°C and could be a potential way to purify and concentrate at the same time, even if only for solvent value. Some of the other work on acids and furfural products is very interesting and may have unique value. There are too many process steps from 2,3-BDO to MEK to fuels. The economics, in my opinion, will not be achieved.

- The CUBI program is a comprehensive effort aimed at selective upgrading of sugars or intermediates prepared by the biological fermentation of sugars. The program is a necessary complement to thermal pathways. Key focus areas are BDO, carboxylic acids (e.g., butyric), and the conversion of sugars to furanics and subsequent upgrading products—e.g., alkane fuels by condensation and hydrodeoxygenation (HDO). There is a lot happening in the CUBI project, and it was, at times, hard to follow a common thread or understand any specific technology platform all that deeply. Considering the diversity of work, it is challenging to cover both the rationale and science on everything in a single talk. The CUBI summary seemed compressed, and it felt like no part of the program got the full attention that it needed. This project may benefit from breaking into four or five subprojects, at least for the peer review presentations.

  Management: The project spans four national labs, so management is critical. The individual research directions at each lab are clearly defined, and there is frequent communication among all partners; however, the CUBI project is expansive, and research thrusts therein are, at times, not directly connected (e.g., BDO upgrading and furan pathways are essentially independent). The specific leadership structure and management hierarchy were somewhat unclear, so I could not really determine if each lab runs independently pursuant to specific goals there or if there is a central point of contact (POC) responsible for coordinating research across the four labs. Cross-project collaborations are well defined, and risks and mitigation strategies are clearly addressed.

Approach: The core focus of this project is on selective upgrading of bio-intermediates as opposed to the less selective pyrolysis and total deconstruction of gasification; therefore, this program is an essential component of the biomass upgrading portfolio. TEA is used appropriately here to guide the program to impactful research. Overall, it seems like a focus on process intensification and utilization of raw feedstocks is more impactful than catalyst development in isolation for model compounds. There is a good focus on catalyst durability here, with emphasis on inhibitor mitigation. This gives a clear idea of purity specs for each part of the process, may reduce separation and purification burdens, and should lead to process intensification and integration. To this end, the collaborations with separations consortia are appropriate.

Impact: This program is significant as an essentially stand-alone project that looks at nonthermal conversion and upgrading strategies, so it covers an important space in biorefining. The team is publishing/presenting/patenting on par with expectations.

Progress and outcomes: I was impressed by a clear demonstration of a BDO to olefins/diesel/jet fuel, particularly for a single-reactor strategy (direct BDO to jet). The team has also identified a potential coproduct in MEK, which is reasonable. The team has mapped out a comprehensive cascade of processes that can be initiated with BDO, leading to a slate of fuels and chemicals. One can view this as a BDO platform chemical model similar to those that have been proposed for HMF, furfural, levulinic acid, etc. The reactive separation strategy (using dioxolanes) is potentially attractive. BDO is a potentially valuable product. Its potential is enhanced by a facile, low-cost separation strategy to allow its recovery from dilute media. The team has done good work on the fundamental chemistries/catalysis involved in BDO-to-butadiene technology. The current risks in the HMF/furfural platform were not clearly specified. Considering the large body of work in this area, I was curious to learn more about the current technology needs here and where additional research is necessary.

- The key goals of the CUBI project are presented on the quad chart (slide 54) to improve the upgrading of key intermediates by doing integrated R&D. The measurement for improvement was given quantitatively as a 25% reduction in the process design cost estimates, along with an MFSP estimate <\$2.50/GGE, including lignin conversion. Other metrics include finding >25% of the valorization revenue in non-lignin-based pathways. The baseline for the cost reduction target was defined on slide 7 as the 2019 SOT at \$7.79/GGE and \$8.20/GGE for the BDO and organic acid pathways, respectively. The management plan was clearly outlined on slide 18, with the critical roles across the national labs defined, noting monthly project meetings and frequent interactions. Excluding NREL, most of the lab partners are focused on the BDO pathway, which is a strategic use of targeted resources to solve the problem. There appears to be some redundancy in catalysis and fuel property testing. The high-throughput screening (HTS) work at PNNL should be highly leveraged to accelerate this project. The team did an excellent job of disclosing critical risks and mitigating actions, such as (on slide 19) water impact, catalyst inhibitors, coke buildup on catalysts, as well as (on slides 8–11) for each pathway. The key end-of-project milestone provided on the quad chart was basically the same as the project goal. There were several cross-project interactions that were good to see, such as scale-up, integration, and separations.

  The CUBI team is highly collaborative within the BETO framework. No IABs or industry engagement were identified. The team tries to have regular meetings to make sure data are exchanged and critical knowledge is shared in a timely way. There is not a clear SOA, and one should be defined in this project, although sequential organic chemical process synthesis is a well-established approach. The SOT goes back to 2017 and used the 2019 SOT to set the targets for the latest AOP. The TEA was used to advance the SOT and set the R&D targets. The team showed a good example using BDO dewatering MFSP sensitivity. This approach is used for each pathway and fits perfectly into the BETO model and goals. This large project supports and advances the BETO and technology area mission of developing and demonstrating transformative and revolutionary bioenergy technologies for a sustainable nation, as well as the BETO goals to develop commercially viable bioenergy and bioproduct technologies.

The CUBI project supports the EERE Strategic Plan goal of enabling a high-performing, results-driven culture through effective management. The project advances the Strategic Analysis Goals to ensure high-quality, consistent, reproducible, peer-reviewed analyses; to develop and maintain analytical tools, models, methods, and data sets to advance the understanding of bioenergy and its related impacts; and to convey the results of analytical activities to a wide audience, including DOE management, U.S. Congress, the White House, industry, other researchers, other agencies, and the general public. The CUBI project supports and advances the Conversion R&D specific, measurable, attainable, realistic, and time-related (SMART) goal by 2021, completing the R&D necessary to set the stage for a 2022 verification that produces both fuels and high-value chemicals to enable a biorefinery to achieve a positive return on investment. The project addresses several key barriers in Synthesis and Upgrading—Ct-H. Efficient Catalytic Upgrading of Sugars/Aromatics, Gaseous and Bio-Oil Intermediates to Fuels and Chemicals; and Integration and Intensification Challenges—Ct-J. Process Integration—identifying impacts of inhibitors and fouling agents on catalytic and processing systems. In support of the Synthesis of Intermediates and Upgrading initiatives, CUBI seeks to transform intermediate streams into stable product streams that meet offtake standards. Finally, CUBI supports and advances BETO’s push for novel technologies by pursuing research on innovative technologies that can broadly enable the conversion of feedstock to fuels and products.

The upgrading and valorization of biochemical intermediates continues to be a cornerstone approach for bioenergy R&D professionals across several industries. The more innovative aspects of this approach upon application will be the engineering solutions to deal with impurities from using real, raw biomass feedstocks and developing the process engineering specifications for key streams in order to protect downstream equipment. These solutions will not be boilerplate but most likely creative adaptations of proven process design approaches. A lot of the key innovation was already accomplished by tweaking the metabolic pathways in the biological strains to produce specific streams in high yield. The CUBI project team seems to understand well how their work will impact the supporting literature within BETO and the external R&D community by publishing 11 peer-reviewed articles along with several patents. The impact on other CUBI external stakeholders (e.g., bioenergy industry, fossil fuel industry, chemicals industry) was brought to the forefront on the impact slides. The technology developed has been leveraged across several industry partners, in particular the sustainable jet fuel work.

The project has an enormous amount of commercial potential, especially in the coproduct biochemical space. The way in which industry has been engaged seems to be through a technology transfer-type relationship, with both the Technology Commercialization Fund and FOA awards for converting acids to biojet fuel and all of the licensing activities that have taken place. One of the more impressive aspects of the progress on this project has been the focus on the BDO pathway. The vapor-phase work at ORNL in the presence of hydrogen demonstrated high conversion and selectivity to olefins using surrogate feeds with spiked impurities as well as tuning capability for MEK coproduction. Coke tolerance was improved using pillared materials flows through industry (MFI) structures using *in situ* thermogravimetric analysis. The corresponding microreactor runs should be shown to further demonstrate the thermogravimetric analysis results. The impact of water at 40 wt %, acetoin, and acetic acid were determined showing negative effects from acetic acid on olefin selectivity. PNNL worked the acid catalytic path via MEK to create olefins. The impact of hydrogen for increasing yields was verified. It would be interesting to see the composition of the spent hydrogen stream. The iso-butanol coproduction adds value to the overall process. The CUBI team made good progress investigating the analytical technique for extracting BDO reactively from dilute water through the dioxolane intermediate and showing additional chemical transformation opportunities from that intermediate. 1,3-Butadiene coproduction via a single-step BDO conversion pathway was presented. Additional catalysis work taking a single carboxylic acid feed and completing a reductive etherification step to produce 4-BH was investigated using a single-phase catalyst at improved yields. With respect to demonstrating improvements consistent with a cost reduction from 25% to 33% for the BDO pathway compared to the FY 2019 SOT of $7.79/GGE, achievement of this milestone appears to be challenged at the moment. The project risk mitigation plan was not mentioned or activated directly. There is quite a bit of pathway investigation ongoing, which appears to be the mitigating actions.

- This is a very complex, interrelated collection of projects. I am glad to see that both chemical and fuels products are under study. It is a good idea to work backward from “allowed cost for this process” to identify the portion to work on and its target within the overall process. Success is well indicated by papers, patents, and industry interest.

  BDO to olefins: Cu/BEA tested? Cu-P-MFI was shown stable for 100 hours. Fixed or fluid bed? Attrition resistance? BDO to MEK: Evaluated impurities—was raw BDO broth tested? Extraction of BDO to dioxolanes: Do dioxolanes have any applications, e.g., solvent? Did you determine if any metals were still in the “cleaned up” broth (with some catalyst deactivation)? BDO to butadiene: achieved 50% yield—what was the target? Butyric acid to ketones: near-theoretical yields. Each project in this program could, and should, be the subject of a longer review. The current arrangement does not permit proper review of the science/progress of the separate projects. It was hard to judge the progress given the short presentations; it looks okay, but it was hard to dig in.

- This is a very comprehensive project including many research subjects that can be independent projects themselves. The team takes the challenge and progresses significantly in quite a few directions. The research of coproducts indicates an interesting direction and may pave a new avenue for the conversion of biomass. It could be beneficial if more efforts can be taken in this direction to explore if it is possible to produce more high-value products based on biomass and how the design of catalysts can help achieve this.

PI RESPONSE TO REVIEWER COMMENTS

- We appreciate the recognition of the recent progress made within this project. While we are aware of 1,4-BDO use as solvent, we have not found industrial application as a solvent for 2,3-BDO. We found that it is typically converted into MEK, which is itself used as solvent. The global 1,2-propanediol market is equal to 2.7 million tons/year (2020). It is not a large market, and, as such, if 2,3-BDO were to replace 1,2-propanediol as a solvent, an excess of 2,3-BDO would still be available. This excess 2,3-BDO could be used for fuels and chemicals production. Catalytic upgrading of 2,3-BDO to solvents or other products and fuels can help to expand its market application. For such applications, purity is very important, so separation and purification as needed to meet specification for use as a solvent could represent a major cost that requires further investigation. Note that most of the required cost reduction needed to achieve overall fuel cost targets are associated with other steps within the overall biochemical conversion pathway, with lignin coproduct valorization being that largest improvement needed.

  The specific catalytic upgrading of sugar-derived intermediates is the focus of this project and requires a 25%–33% cost reduction in the catalytic upgrading operation relative to the starting point in 2019. Our mid-project and end-of-project milestones are directly associated with this metric, and we are demonstrating the required cost and performance measures needed to achieve this progress using biomass-derived process streams in an integrated manner.

  We are also developing catalytic upgrading approaches to target higher-value coproducts from such intermediates to lessen the exclusive dependence on lignin-derived coproducts to enable fuel cost targets. Many techniques have been envisioned and applied by others to separate/extract 2,3-BDO, including conventional distillation and crystallization, but, to the best of our knowledge, none of them has yet found commercial application due to large energy requirements. We note that a small effort is conducted under this project to separate BDO from the broth because it is a novel technique using organic chemistry; however, non-chemistry separation techniques are not the focus of this project, but they are being investigated in collaboration with the Bioprocessing Separations Consortium. Unlike other approaches, the two-step approach for converting 2,3-BDO to olefins fuels precursors via MEK allows for:

  - The use of catalysts with hydrothermal stability that are tolerant to highly diluted feedstocks (i.e., 90 wt % water). This is important because the 2,3-BDO fermentation broth is highly diluted in water (~90 wt % water), and separation of 2,3-BDO from water remains challenging and energy-intensive. Significant research efforts are still needed to allow for the economic separation of 2,3-BDO from water. By using an aqueous feedstock where 2,3-BDO/water separation is not needed, we de-risk the process compared to other approaches.

  - Coproduct diversification beyond MEK. Coproducts are needed to reduce the dependance on lignin upgrading to adipic acid. MEK is a possible coproduct, but other coproducts will be beneficial because the MEK market is small (global: 1.7 million tons/year) and would quickly become saturated.

- We appreciate the comment regarding the wide breadth of activities being conducted within the CUBI project. There are many advantages for all of the catalytic upgrading efforts within the broader biochemical conversion pathways to be performed within a single coordinated effort that spans work at several national labs, which was the approach recommended approximately 6 years ago—before which these efforts were conducted as individual projects in a less coordinated manner. The current management structure involves a central coordination effort at NREL, where much of the associated process development and TEA support for the overall biochemical conversion pathway is conducted. Although the format for the peer review presentations is more of a broad programmatic overview of the project and not a deep technical presentation, we recognize the difficulty for the reviewers to assess the specific technical approaches of each project activity in the current format, and we will consider other ways to allow for a more thorough technical review in the future. It is gratifying to see the recognition of inhibitor mitigation as a major crosscutting thrust in the CUBI project because this was specifically chosen as an area for emphasis at the start of the current 3-year project cycle in 2019. A major outcome of this project will be to understand the catalytic upgrading feed-stream specifications and associated purification/separation requirements as related to the upstream deconstruction and biological conversion steps utilizing raw biomass feedstocks. We agree that there is a large body work on production of furfurals and aldol condensations and some work on the production of hydrocarbons from biomass sources. Our approach differs in that our goal is to develop a simple process that minimizes the number of separations required and to process the whole hydrolysate (hexoses and pentose sugars) through to hydrocarbons in a continuous process. In addition, the ketone used in the aldol condensation is bio-derived MEK, which is less reactive than other ketones, such as acetone or cyclopentanone, but it does introduce branching in the final hydrocarbon product, so that it has a low-temperature cloud point and is thus suitable for blending into jet and diesel fuels.

- Coproduct opportunities have been emphasized in a greater manner in this project during the last 2 years to lessen the exclusive dependence on lignin-derived coproducts in biochemical conversion pathways to enable fuel cost targets. Additionally, utilizing corn starch-derived hexose sugars in existing corn ethanol commercial plants can provide a near-term opportunity to repurpose such facilities away from ethanol production to produce higher-value product revenue streams using existing commercial-scale fermentation capacity.

- Regarding the BDO-to-olefins approach, we did test Cu/BEA, but we did not include those results in the peer review presentation. Cu/P-MFI was tested in a fixed-bed reactor, so we did not focus on the attrition resistance in this system. Regarding the BDO-to-dioxolanes approach, we have found that the dioxolanes are prone to oxidation over time and/or if exposed to heat and air, which could preclude any use as a solvent. Residual metal in the broth after pretreatment was measured, and we were unable to detect any remaining metals by inductively coupled plasma mass spectrometry. We recognize the difficulty for the reviewers to assess the specific technical approaches of each project activity in the current peer review format, and we will consider other ways to allow for a more thorough technical review in the future.

- Fuel property testing capabilities that already exist at the national labs involved in the CUBI project have been utilized to quantify key fuel properties for the fuel products generated from the catalytic upgrading approaches that are being developed. This includes using certain unique capabilities present at a given national lab to measure fuel properties from upgrading approaches being developed at other national labs in a consistent and collaborative manner. We appreciate the recognition of the importance of developing integrated engineering solutions to address impurity considerations when using biomass-derived process streams in catalytic upgrading reactions. This has become a key area of emphasis in this project and represents an advancement from lower-TRL activities during early years of the project that used model compounds and/or mock hydrolysates/fermentation broths to the current higher-TRL efforts using process-relevant streams from real biomass deconstruction and fermentation operations, where we are developing an understanding of how these upstream processes affect the quality of the streams being fed into the catalytic upgrading reactions. Performing inhibitor identification and catalyst poison studies and determining their impacts on catalyst lifetime, regeneration, and feed-stream cleanup requirements provides significant insights into optimizing this critical process integration interface. The importance of 2,3-BDO as an upgradeable intermediate is largely related to the ability to produce it from mixed sugar biomass hydrolysates at extremity high fermentation product titers (>100 g/L), making it one of the primary pathways being developed within BETO's broader biochemical conversion portfolio. The CUBI project represents the primary effort within this broader portfolio for catalytic upgrading of this intermediate to diesel/jet fuel molecules/blendstocks and large-market chemical coproducts. During its lifetime, the CUBI project has progressed from catalyst and process development on model compounds to its current emphasis on real process streams in a fully integrated process context. The requirement for a 25%–33% cost reduction in the catalytic upgrading operation relative to the starting point in 2019 was determined by TEA modeling efforts to identify catalytic upgrading improvements that are needed to achieve these cost reductions, assuming all other areas of the broader biochemical conversion pathway are also able to achieve their targeted improvements, including coproduct valorization of lignin. Collectively, all of these improvements will result in achievement of the targeted MFSP cost target of $2.50/GGE by 2030. Our mid-project and end-of-project milestones are designed to determine which approaches appear to be able to (or not able to) achieve the catalytic upgrading portion of the overall cost reductions and allow for rescoping of resources within the project to best achieve this outcome.

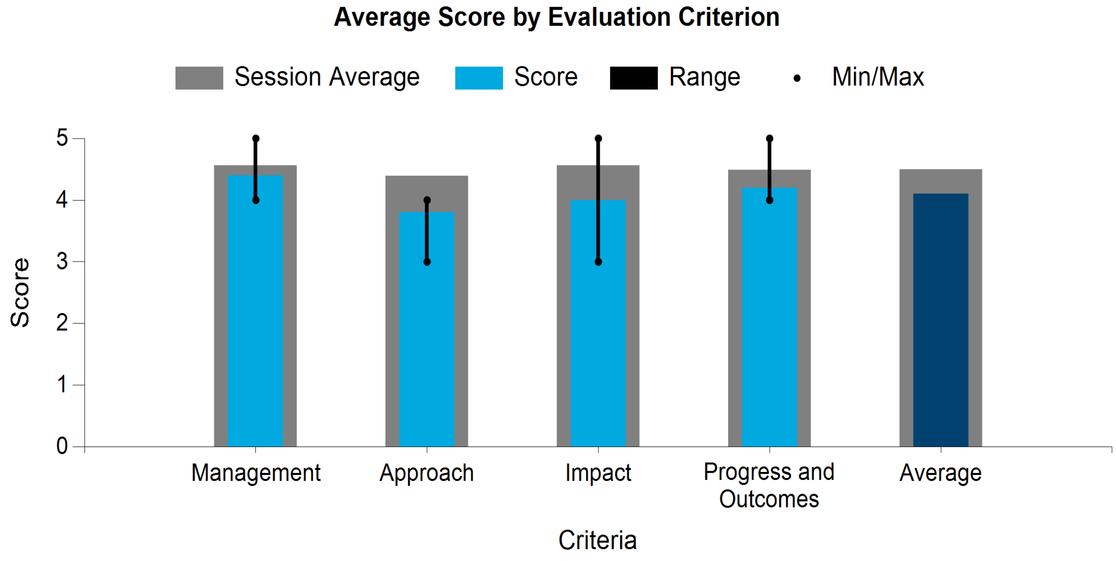
CATALYTIC UPGRADING OF CARBOHYDRATES IN WASTE STREAMS TO HYDROCARBONS

North Carolina State University

PROJECT DESCRIPTION

WBS:	2.3.1.209
Presenter(s):	Sunkyu Park; David Johnson
Project Start Date:	10/01/2018
Planned Project End Date:	12/31/2021
Total DOE Funding:	$2,475,807

The primary objective is to develop a technology for converting the carbohydrates in paper sludge, a wet organic industrial waste stream, into a hydrocarbon biofuel, both economically and sustainably. In the United States, more than 8 million wet tons of paper sludge (50% moisture) are generated annually. Most of it is landfilled at an approximate cost of $240 million per year, including trucking and landfilling costs. This material contains readily digestible carbohydrates, which can be used for product development. This project will develop an integrated process using wet paper sludge, where no drying of the feedstock is needed. The process includes (1) ash removal from paper sludge, (2) enzymatic hydrolysis of carbohydrates to monosaccharides, (3) dehydration of sugars to furans, (4) aldol condensation of furans with ketones to intermediates having molecules with 14–16 carbons, (5) HDO of the intermediates to paraffins with excellent properties for blending in a jet or diesel fuel, and (6) robust TEA and LCA to focus research on developing cost-effective routes to address key cost barriers and ensure the sustainability of the process. The process will be integrated and optimized, and a potential to achieve a minimum 25% reduction in the net levelized cost of disposal of the paper sludge will be demonstrated. Finally, the developed process will be validated at a relevant scale to produce sufficient hydrocarbon product for fuel property testing.



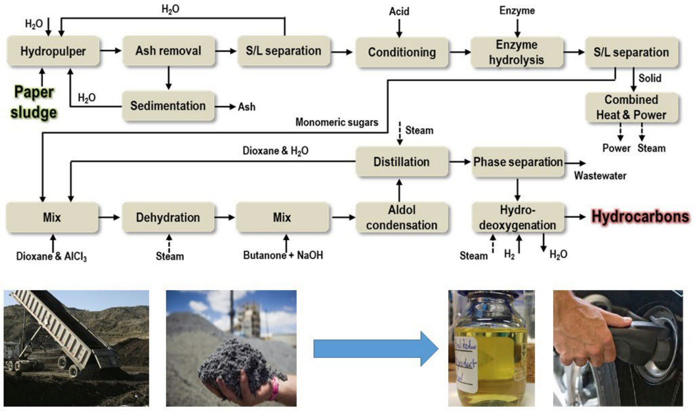


Photo courtesy of NCSU

COMMENTS

- Excellent management of the program, which is complex, with all the various aspects of materials to convert. The team did a good job showing the build from previous work on model systems. The approach using paper waste is solid, with no foreseen issues other than concern over the amount of hydrochloric acid utilized and the waste stream generation from the use of hydrochloric acid. This could be substantial because hydrocarbons produced after aldol condensation are branched. In the detergent industry, a feedstock with methyl branching could have input into the surfactant market for higher value due to the performance and green technology aspects with consumers; however, aldol is an expensive process, so there is concern over meeting economic goals longer-term to make higher-value fuels, but as stated, it still may have chemical value to industry. This shows solid progress and outcomes, and, as such, I see no major issues.

- The key goals of the NCSU project are presented on the quad chart (slide 27) to convert pulp and paper sludge into hydrocarbons economically and sustainably. The quantitative targets for the economics and process KPI targets are not mentioned. The project had clear lab-scale, milliliter-quantity milestones and deliverables in each year to produce furfural and HMF in the first year, produce hydrocarbons in the second year via aldol condensation and HDO, and scale up the product to liter quantities in year three. The critical project tasks and roles are assigned clearly between NCSU, NREL, and Yale. The team did a good a job of identifying several big risks—namely, sludge ash concentration, catalyst deactivation, and sludge quality control. The mitigation actions seem reasonable—adding more sludge pretreatment units, characterizing catalyst deactivation and solve with both a scientific and engineering solution, as well as optimizing the process based on one specific sludge stream or feed slate. The milestones were clearly outlined on slide 7 with the go/no-go occurring this summer, delivering 50 mL of hydrocarbons, of which 50% can be blended directly into distillate, and a 25% reduction in the levelized disposal cost. The communication plan was clearly laid out with monthly calls between NCSU and NREL, quarterly reports, frequent interaction with BETO, and face-to-face BETO validation meetings. There appears to be no IAB or direct industry partner engagement on this work, which is a strong desire for this work, at a minimum, to keep a steady supply of real sludge feedstocks. This gap should be fixed easily by leveraging the BETO IAB community. The team has contacted many sludge producers at this point. There was an explicit approach outlined that does not compare to any SOA converting paper sludge to fuels. It was mentioned that this is an alternative to anaerobic digestion routes, so a baseline block flow diagram of the SOA could be helpful. It appears that some original work was done as organic synthesis using autoclaves to verify the most critical liquid phase transformations followed by HDO. Once the lab-scale basic chemistry was proven with key model compounds representing the constituents in paper sludge, then a block flow diagram was developed. This is the classic process development heuristic across the chemical industry throughout the decades. The approach generally involves the use of real streams at some point, which was used here, taking samples from the sludge survey. It also seems like some catalysts are involved here. It is not clear if these are homogenous or heterogeneous, recoverable or irrecoverable. The project supports the BETO and technology area mission of developing and demonstrating transformative and revolutionary bioenergy technologies for a sustainable nation, as well as the BETO goals to develop commercially viable bioenergy and bioproduct technologies. The project supports the Conversion R&D SMART Goal by 2021, completing the R&D necessary to set the stage for a 2022 verification that produces both fuels and high-value chemicals to enable a biorefinery to achieve a positive return on investment. The project addresses several key barriers in Synthesis and Upgrading—Ct-H. Efficient Catalytic Upgrading of Sugars/Aromatics, Gaseous and Bio-Oil Intermediates to Fuels and Chemicals and Integration and Intensification Challenges. Overall, economically turning a paper sludge stream into sustainable jet fuel has great innovation potential. The approach may not be the most innovative to accomplish this feat due to the number of synthesis steps required. Nevertheless, the pathway could be a viable route for BETO in the future. The team appears to understand the size of the opportunity based on the quantity of sludge available across the United States and its impact for BETO. The project's impact on the bioenergy community at large seems limited. The project has great commercial potential for a number of mills and paper companies that can be engaged. The team contacted 17 companies to complete a sludge survey, and 11 types of sludge samples were received. Unfortunately, the project was unable to secure an industry partner that could help commercialize the work. The team has made considerable progress with lab-scale process development activities toward the overall goal. More than 93% ash was removed, keeping >65% of the carbon, with the carbohydrates mostly characterized as glucan and xylan. Batch enzymatic hydrolysis of the glucan and xylan to produce sugars showed high yields along with dehydration to furans in the presence of dioxane solvent and aluminum chloride catalyst using a microwave reactor. The commercial scale for this step will obviously look different and may be carried out in a more traditional fashion using more costly, slower, batch methods. The theoretical yields for adducts formed from condensation chemistry by adding MEK and caustic were almost reached. The purchase of MEK and caustic impact must be included in the final TEA. The team completed all of the steps except HDO, which had already been done in previous work with model compounds. Almost all the milestones for the go/no-go have been reached, except the lower chemical oxygen demand reduction, which is critical for the project goals. The risk mitigation actions or contingency plan for this remaining task were not discussed. The HDO work is going very smoothly at NREL, with no issues.

- This project aims to convert carbohydrates of paper sludge to hydrocarbons. The whole project is divided into two parts: sludge to furans and sugars to hydrocarbons. The team is using TEA and LCA to guide their research. The team has a monthly conference between the two major participants, NCSU and NREL, and it would be helpful if the management also presents how the participants at Yale are involved because the Yale group does the TEA and LCA, an important part. It could also be beneficial if the team could consider strategies of reusing enzymes because they are pretty expensive.

- This project investigates multistep processes for recovering chemicals from paper sludge. The presentation was very well organized and clearly presented. What were the overall economics? (Answer: $3.60/GGE.) The paper sludge could be a good feed for steam reforming in a solids contacting reactor because the fillers (Ca, Mg, Fe) help catalyze the pyrolysis process at modest temperatures.

- This project is a collaboration among NCSU, NREL, and Yale that is focused on utilizing wet waste from pulp and paper, specifically paper sludge. My understanding is that paper sludge has short fibers and high ash content, so it is low value and difficult to upgrade. Presumably, it is then slated for treatment/disposal, so it would be a large cost for a pulp and paper facility. The objective here is to produce hydrocarbon biofuels from paper sludge, generating 1 L for fuel property testing at a 75% blending level with petroleum diesel or jet fuel.

Management: The roles of each partner are clearly established and appropriate according to expertise. Importantly, the team has involved pulp and paper industry at a large scale, so there is good interaction with stakeholders. Regular communications occur internally, as well as with project managers within BETO. The team has clearly identified risks and provided reasonable mitigation strategies, and they have established clearly where they stand with respect to intermediate milestones for the project. No major weaknesses are evident with respect to management.

Approach: This project outlines a cascade approach to paper sludge upgrading, going through ash removal, enzymatic degradation to monomeric sugars, catalytic dehydration to HMF and furfural, condensation of furanics with MEK, and HDO to jet diesel-range components. This is a classic furan-to-diesel-type pathway. The great challenge here is probably ensuring adequate performance in the presence of impurity carryover using a paper sludge feedstock, so the effort in process integration seems appropriate. Although the team indicates an ability to recycle the dioxane solvent, there may be concerns with respect to toxicity and/or cost in being able to scale the process. That said, it is unclear that there are better solvent options. An advantage of dioxane may be that it is low boiling relative to dimethylsulfoxide, which may help with purification of furfural and HMF. Tetrahydrofuran may also have been an option. It should be less toxic and potentially biomass-derived. The related project from Wyman and Cai demonstrated good results with that platform. I was not clear on the standing research challenges in synthesizing furfural/HMF or in condensation and hydrotreating, and how they differ in this project relative to other efforts. Presumably, the major one is the carryover of impurities?

Impact: The team is forecasting impacts in the reduction of environmental waste disposal, the reduction in waste-handling costs for the paper industry, and the production of renewable fuels. This is a good example of the utilization of cost-advantaged feedstocks, like paper sludge, which currently represent a disposal cost. It is worth pointing out that this technology is a natural fit with existing paper mills, suggesting the possibility of leveraging current infrastructure to reduce capital investment required to move the technology to scale.

Progress and outcomes: I like that the team is working directly with pulp and paper companies to handle actual paper sludge instead of doing work on, for example, microcrystalline cellulose or even raw biomass. As I see it, working with a relatively low-grade feedstock is one of the biggest challenges here, so efforts in ash removal and achieving high yields of sugars, HMF, furfural, etc., in an integrated process is necessary considering the impact of inorganic species on enzyme and catalyst activity. There has been considerable TEA of related systems done in the past 10 years or so, and it seems that economic viability always comes down to solid content, dioxane ratio, and solvent loss. It is not clear what research is needed to further improve upon the SOT with respect to furfural-to-alkane strategies.

PI RESPONSE TO REVIEWER COMMENTS

- The project team thanks the review panel for their encouraging and thoughtful comments, as well as their recognition of the work progress, management, and potential impact. Based on the reviewers' comments, we will evaluate different solvent systems (e.g., tetrahydrofuran), enzyme reuse, and the impact of hydrochloric acid use in wastewater treatment. We will also investigate the possibility of product development for the surfactant market. We will continue to work with our stakeholders, such as the pulp and paper industry.

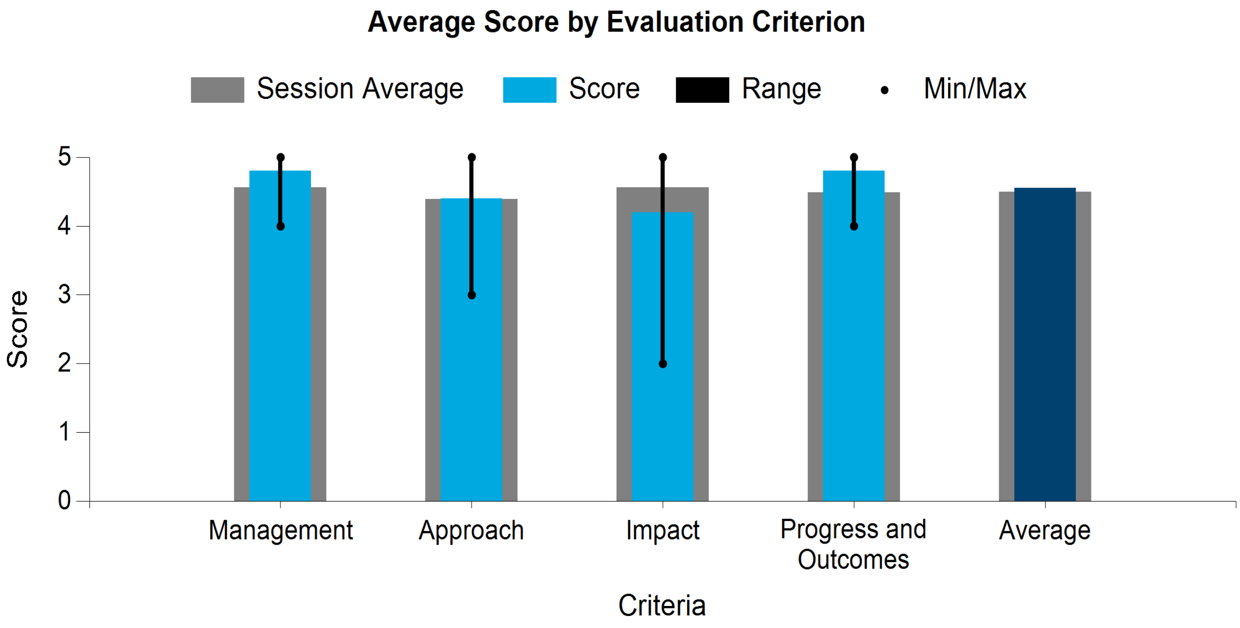
UPGRADING OF C2 INTERMEDIATES

Pacific Northwest National Laboratory

PROJECT DESCRIPTION

WBS:	2.3.1.304
Presenter(s):	Rob Dagle; Asanga Padmaperuma; Corinne Drennan
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2022
Total DOE Funding:	$2,250,000

We are developing new catalytic upgrading technologies that enable cost-competitive conversion of C2 intermediates (including ethanol), produced either thermochemically or biologically, to highly desirable jet or diesel blendstocks. We aim to develop a commercially viable process within the concept of an integrated biorefinery—a smaller production scale than petroleum refining, with lower-capital-cost fuel synthesis, and provide control over the product distribution such that process operation can be adjusted to meet market demand. The coproduction of value-added chemicals may also improve overall economics as well as provide feedstock flexibility for commercial operation, and this is being investigated in tandem with fuel products. TEA is used to define technical targets and evaluate research progress toward ultimately demonstrating the processes. Efforts have culminated in the discovery of a new catalyst system for the direct conversion of ethanol to n-butene-rich olefins. This pathway provides an economic route to jet- and diesel-range hydrocarbons over the current SOT, with the elimination of a unit operation and additional energy savings enabled by coupling exothermic and endothermic reactions. The project team has recently begun to scale up the patented catalyst technology developed on this project, employing modular microchannel reactors, teaming with LanzaTech and Oregon State University to take it a step closer to commercialization.



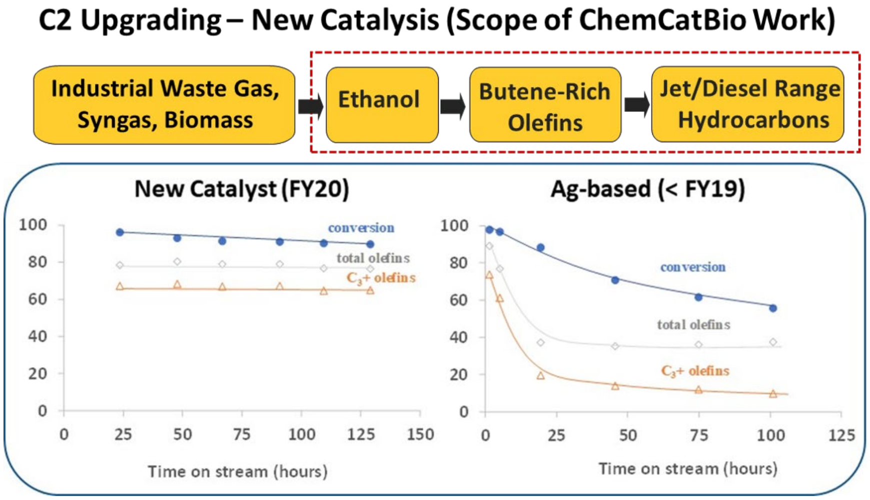


Photo courtesy of PNNL

COMMENTS

- The focus on risk management explicitly is a good approach. Since butene coproduct is key to the economics, it is good that most of the effort is going into this target. The projections of costs on slide 16 seem to indicate that one can *never* reach \$3/GGE. Slide 18 seems to indicate that butenes are "unfavorable." Understanding the impact of silver dispersion and acid site concentration is very important; what do you do with this? Are oxide supports favored compared to carbon or other nonpolar supports? The approach of using the mechanistic insights to direct work is particularly impressive. The new catalyst performance shows the impact of using mechanistic insights to improve catalyst performance. Are you familiar with the Celanese work on ethanol upgrading to all sorts of chemical products (e.g., ethyl acetate), not fuels? They have numerous patents.

- There is no issue with the catalyst development program management. The management has done a great job working with the team to advance the progress of the ethanol-to-olefins work. The catalyst approach for ethanol conversion has been well thought out, and the development is successful. The main issue is the current economics of cellulosic ethanol, at \$3.80/GGE, not the catalytic work by the team. I like the idea of starting with the existing ethanol production from corn until such time that the economics of cellulosic ethanol improved. LanzaTech, I believe, currently has better economics via this route, and perhaps could be another alternative until cellulosic ethanol production can improve economically. I commend the progress on catalyst development from 2017 to this review. Again, I'm struggling with the calculations with the ethanol input at \$3.80/GGE and the catalyst at \$3.40/GGE, or am I misreading the charts? These values indicate extremely high-value coproduct is needed; however, in my opinion, no olefin coproducts will add sufficient value to justify the project unless crude oil price by 2030 is high. Thus, I'm questioning the stated outcome of the potential to obtain a distillate fuel MFSP of \$3/GGE. I do not, however, wish to downplay the team working on catalyst developments, which have future potential in the chemicals industry, as well as fuels, should crude oil reach high prices.

- The key goals of the C2 Upgrading (C2U) project are presented on the quad chart (slide 31) to improve catalysts for ethanol-to-C4 transformations, enabling further oligomerization to diesel-range hydrocarbons. The catalyst improvement targets were not quantitatively mentioned. The TEA was used to drive research direction toward increasing olefin selectivity to an unspecified target. The communication plan was given on slides 10–12, with the work direction between PNNL and ORNL clearly distinguished by catalyst family type, with distillate fuels production as the key objective. There is an academic collaboration with Washington State University involving fundamental catalysis, support for higher-TRL work, and collaboration with ChemCatBio crosscutting teams. The risk management plan was provided, identifying three critical areas of carbon efficiency, catalyst durability, and process economics. The mitigation actions involve collaborations mostly within ChemCatBio, which could possibly benefit from additional outside partners. The key project milestone involves achieving the $3/GGE MFSP milestone for distillates with KPIs being 100 hours time on stream (TOS) and two regeneration cycle evaluations. Other milestones include the evaluation of additional coproducts on TEA. The team showed how the MFSP has olefin yield sensitivity. The communication plan indicated quarterly communications between PNNL and ORNL as well as other collaborations with enabling projects. The C2U project mentioned the engagement of the IAB during the presentation. The SOA for C2U continues to be the LanzaTech alcohol-to-jet process. The approach is the traditional screen, downselect, and baseline catalyst performance method for material discovery. The approach centers around controlling the olefin intermediate/coproduct distribution as a way of controlling the final distillate product distribution. Generally, this type of effort leads to a more optimized, final, next-generation catalyst family above the catalyst SOA for this project. Further, as slide 19 suggests, it will advance the alcohol-to-jet process by reducing the unit operations and bringing in new coproduct opportunities. The C2U project supports BETO and the technology area mission of developing and demonstrating transformative and revolutionary bioenergy technologies for a sustainable nation, as well as the BETO goals to develop commercially viable bioenergy and bioproduct technologies. C2U supports the Biochemical Conversion Program objectives pertaining to integrated conversion technologies by showing how new catalyst materials are moved into other BETO scaled-up system integration efforts with the recent FOA with Oregon State University and LanzaTech. C2U supports the Conversion R&D SMART Goal by 2021, completing the R&D necessary to set the stage for a 2022 verification that produces both fuels and high-value chemicals to enable a biorefinery to achieve a positive return on investment. The approach is basically to test several of the best catalyst candidates and check the TEA for the corresponding conceptual process design impact. The team is aware of the potential of ethanol as a critical chemical processing building block intermediate molecule, particularly when the market prices swing away from motor gasoline fuel-blending incentives. C2U has the potential to optimize and reduce the design costs for the alcohol-to-jet process, which is already commercially licensed. C2U catalyst scale-up with LanzaTech and Oregon State University via a BETO FOA is ongoing, along with MCPI efforts using microchannel reactors for building energy efficiency into the process. This process has quite a bit of potential to go commercial in the near future. Toward the goal of improving catalysts for ethanol-to-C4 transformations, significant progress has been made and published highlighting these new fundamental insights, such as silver promotion, mechanistic impact, and acid surface C4 product tuning; and atomic layer deposition synthesis for the same catalyst system along with acid strength characterization, deactivation mode elucidation, and 800 hours TOS testing. All of this insight led to an improved next-generation catalyst system with almost an order higher activity and increased stability resulting in a $0.50/GGE reduction in MFSP estimates. Other notable achievements involve computational work by the CCPC suggesting the impact of surface proton concentration as the key mechanistic control phenomena. The key project milestones with MFSP, TOS, and regenerations were partially reached in this last work period. The new generation catalyst had improved stability not yet realized at 800 hours TOS. The regeneration milestone was achieved for coke formation and oxidation state-based deactivation. The process design TEA estimates are heading in the right direction.

- The presentation by Rob Dagle was insightful and rational. Overall, this was a very nice summary of the program. The direct conversion of ethanol to butene is attractive.

  Management: There is good interaction between PNNL/ORNL as well as the IAB. The collaboration structure and individual tasks of the various programs within BETO and university partners are well defined. There is a clear identification of risks as well as a reasonable mitigation strategy that leverages appropriate expertise in each area. There is a well-defined milestone structure. There are no major weaknesses in the management.

Approach: The project is mainly focusing on the direct conversion of ethanol to higher olefins and distillates. The work is guided by TEA, which is appropriate for directing effort toward impactful research. This team showed TEA without coproduct credits, which made it much easier for me to see the impact of the work here. I think the team has made a good choice to upgrade carbonyls by aldol condensation instead of using ketonization to upgrade acids. It should be more carbon-efficient and happen under milder conditions, provided that one can avoid carboxylic acid formation in the first place. There is a good focus on process intensification and moving to a smaller scale to be compatible with biomass processing at distributed scales. There has been a reasonable benchmarking effort to establish the base case of the technology, and a shift from ethanol-to-ethylene to ethanol-to-C3 is attractive because it is much easier to make long-chain, branched hydrocarbons from C3 olefins than it is from ethylene.

Impact: The ethanol focus is a good choice due to the increasing supply/decreasing cost of biogenic ethanol, as well as blend wall restrictions. Ethanol is certainly a reasonable source for fuel or chemical production, provided that its upgrading is cost-effective. So the catalysis focus here is appropriate. The alcohol-to-jet collaboration with LanzaTech has already demonstrated a successful application of bio-based jet fuel. Ongoing and future focus on process intensification may help to make this ETJ pathway more feasible. The team is exploring scaled-down reactors and additive manufacturing, which hints at feasible distributed-scale implementation.

Progress and outcomes: The work here has outlined the mechanism of producing butene from ethanol over Lewis acids. There has been good utilization of *in situ* nuclear magnetic resonance leveraging unique capabilities at PNNL. Their mechanism/pathway analysis is instructive on how to manipulate operating conditions to improve selectivity/activity. They have found that silver dispersion correlates with conversion, but selectivity correlates with Lewis site density. This instructs the design of a more active/selective catalyst. The utilization of atomic layer deposition to obtain monodisperse Zr^4 is interesting, but the origin of its improved performance is not entirely clear, nor is long-term retention of monodisperse zirconium (Zr) during regeneration cycles. Focused investigations into catalyst deactivation identified three mechanisms of deactivation. This has informed subsequent mitigation and stabilization strategies, resulting in a more stable catalyst. Improved coke resistance is attributed to avoiding intermediate formation of butadiene, which seems reasonable. This project has appropriately leveraged computational capabilities to develop a fundamental understanding of selectivity/stability differences between past and current catalysts.

- This project aims to develop catalysts and an economically viable process that can produce fuels based on the chemical conversion of ethanol. The research shows significant advancement. It is very impressive that the team collaborates with several enabling groups to conduct a comprehensive study on the mechanisms of catalysts. The idea of valuable coproducts could be an important concept for the biorefinery to produce fuels. A similar strategy of coproducts has been utilized by several other groups. The selection of coproducts seems to be very important. It would also be interesting if the balance between fuel and coproduct can be used to guide the design of the catalysts.

PI RESPONSE TO REVIEWER COMMENTS

- The insightful comments provided by the reviewers are greatly appreciated. The project team is encouraged by the positive statements made by the panel about the progress made with the catalyst development. The positive comments made on the importance of controlling the formation of olefin intermediate and coproduct distribution as a means for controlling the final distillate product distribution are well received. The strength of the collaboration with different teams across the consortium, including computational capabilities, and with our academic partner was also noted. One reviewer applauded our mechanistic approach utilizing aldol condensation for carbon-carbon coupling versus ketonization as a more carbon-efficient route. It was also noted how the generation of coproducts is an important concept for biorefineries in fuel production.

Regarding the comment on how the balance between fuel and coproduct can be used to guide the design of the catalysts, we certainly agree with this point—and the production of different coproducts is something that we intend to investigate further in the future. We believe that the types of multifunctional catalysts being developed here could be adapted for other product opportunities. Note that we are nominally aware of the Celanese work on products from ethanol. We will incorporate this comment in the future scope.

Questions were raised around the catalyst targets, TEA, and with the more fundamental catalysis being performed by our academic partner. These points are clarified and addressed below. Regarding the comment that catalyst improvement targets were not quantitively mentioned, we would like to point out that in the approach on slide 16, we showed how, according to our model, the MFSP cost target could be met assuming that 95% carbon selectivity to the olefins can be achieved and assuming n-butene coproduct was taken. This is our end-of-project target. We also had a mid-project catalyst performance target milestone of 90% total olefin and 65% C3+ olefin selectivity, which was recently met, as shown in the approach on slide 17.

Regarding the comments on TEA, we apologize for the confusion, which is really due to the fact that there are two separate process models—one for PNNL's catalyst (Task 1) and one for ORNL's catalyst (Task 2). For the PNNL catalyst, the process model assumes thermochemical conversion of forest residues to ethanol, which utilizes a more recently updated biomass feedstock cost (which lowers the production price of ethanol). The model for the ORNL catalyst was developed based on biochemical processing of corn stover using data obtained from an earlier 2011 report. There are two different process models because the PNNL and ORNL catalyst programs originated from different sections of the BETO program. In recent years, these programs were combined due to their similar goals around ethanol upgrading, but the same models were kept for consistency. We plan to use a fixed ethanol feedstock cost for both models, and then assess the progress made in reducing the ethanol upgrading costs moving forward. The comment that the utilization of atomic layer deposition as a means to obtain monodispersed Zr^{4+} was interesting; however, the origin of its improved performance was not clear, and the reviewer questioned the feasibility for long-term retention of monodispersed Zr during regeneration. To clarify, we believe that the synthesis of well-ordered Zr sites leads to Lewis acid sites with increased medium strength, relative to weak and strong acid strength, as evidenced by infrared, and this may contribute to the favorable selectivity performance. This is a new finding because before we observed how Lewis acid site concentration, not necessarily strength, is a critical factor. But, certainly, this finding by our academic partner is still early, and we are working to understand more. Further, we agree that longer-term stability of these well-ordered Zr structures is a question. We note that this is just one of the newer approaches being investigated. The mixed-metal catalysts prepared using more conventional synthesis appear to be reasonably stable and regenerable thus far. As suggested, catalyst durability will be more rigorously addressed with longer-term duration studies moving forward.

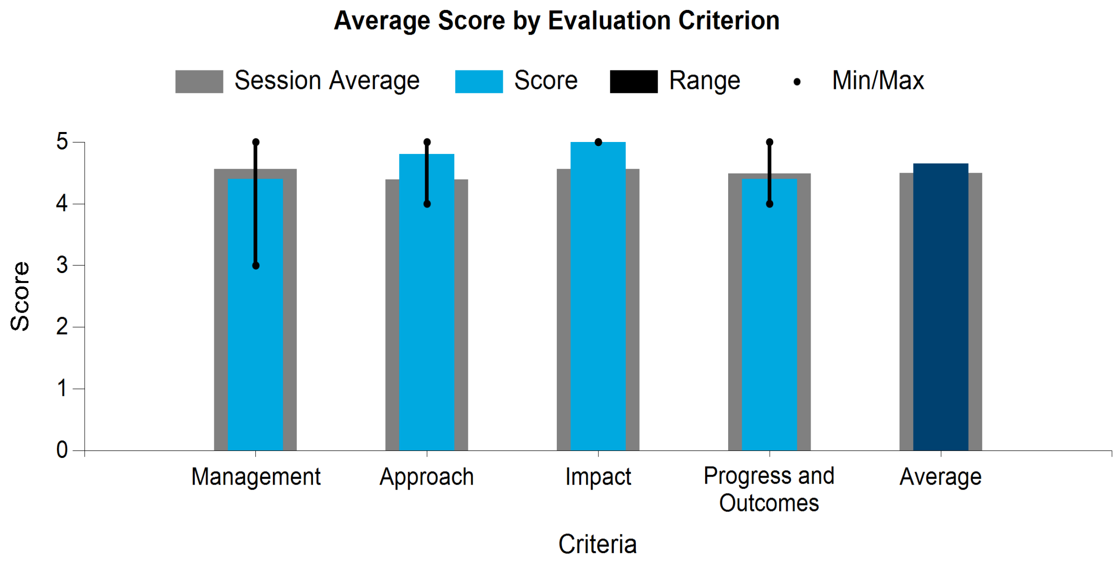
UPGRADING OF C1 BUILDING BLOCKS

National Renewable Energy Laboratory

PROJECT DESCRIPTION

WBS:	2.3.1.305
Presenter(s):	Adam Bratis; Dan Ruddy; Zia Abdullah
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2022
Total DOE Funding:	$3,200,000

This project is developing the centerpiece technology for a market-responsive, integrated biorefinery concept based on the conversion of renewable C1 intermediates (e.g., syngas, CO_2, methanol) to a suite of fuels and coproducts with improved carbon efficiency, reduced CapEx, and control of the product distribution to meet market demand. Advanced upgrading technologies of syngas are critically needed for the successful commercialization of fuel production at a scale relevant for biomass gasification. Research tasks within this project leverage complementary catalyst and process design for the conversion of CO_2-rich syngas (15%–20% CO_2 in syngas) to achieve high-carbon yields of gasoline and jet fuels as the major products. The conversion pathways generate high-quality fuels (e.g., high-octane gasoline with low aromatics, desirable jet-range hydrocarbons) and have the potential to achieve favorable cost targets by 2022. Research progress is compared against the Mobil olefins to gasoline and distillate (MOGD) process, which also offers control over the gasoline and distillate products, as an industry benchmark. The pathway for the direct conversion of CO_2-rich syngas to hydrocarbon fuels seeks to exceed the carbon efficiency of biomass-sourced MOGD (31.8%). Recent catalyst and process development achievements are highlighted by improvements in carbon selectivity to fuels and carbon yields, along with evidence of the incorporation of carbon from CO_2 into the hydrocarbon products.



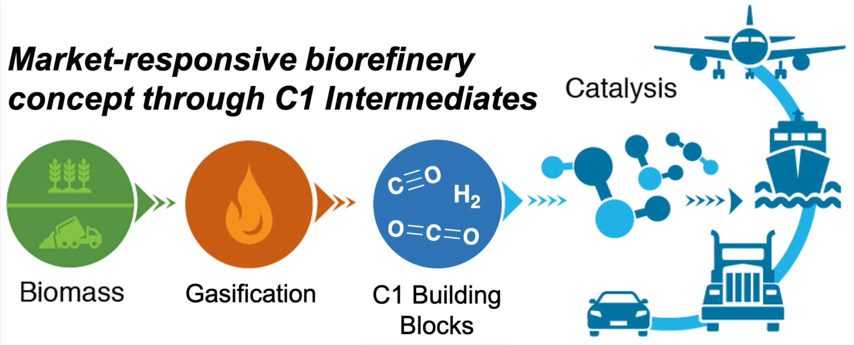


Photo courtesy of NREL

COMMENTS

- The team's progress on challenges speaks to solid management. The systematic approach with feedback from modeling and analysis has great potential in stepping from the three-step process to one step, with continued learning and progress ongoing. I consider the potential of the one-step process to be high, considering the achievements to date on DME to high-octane gasoline and direct syngas work to high-octane gasoline. This could become a key high-volume route, initially to value-add fuels and chemicals as well, due to the focus on the process with branched materials, which have higher octane and perhaps even some chemical reapplications. It can be not only a stand-alone process to jet, but also often fuel companies use these materials as a blendstock to increase the value of the lower-quality fuels as well, which gives it potential to be introduced at lower scaling into the market, allowing more time toward the high production of high-octane gasoline. As stated before, the continual progress of the team stepping from the first approach toward a more efficient one step is outstanding and getting excellent results closer to the $3/GGE target. This year's focus could provide the necessary outcome to meet the goal, and I believe they will have a substantial chance to meet or exceed the goal. The only question I have is that their goal for the coming year is set too low considering the great progress across the various approaches.

  The goal to convert CO_2-rich syngas to high-octane gasoline is lofty, and it has been studied broadly. The current approach was chosen rationally and shows good promise. The use of BEA rather than ZSM5 seems a great choice because Cu/BEA shows a good advantage with respect to peptide nucleic acid production, catalyst deactivation, and regeneration temperature. A very important demonstration is the 500 hours of operation at a larger scale of methanol to gasoline. I appreciate the attack of studying individual steps and the stepwise approach going from syngas to CO_2 only. This is a very well-conceived project. It tempts me to read most of the references (if I had time). I was confused as to what the economic target was for the carbon efficiency for $3/GGE and how the results relate to that. Cu/Zn is a good shift catalyst. Does that present a limit? (Answer: It could.)

- The key goals of the C1 Upgrading (C1U) project are presented on slide 3 and on the quad chart (slide 22) to develop renewable C1 conversion to flexible fuels with improved performance over the MOGD process baseline. There are no quantitative targets on how much improvement over the MOGD is expected. It is assumed that C1 technology would include both the catalyst and process combined. The project team did a good job of laying out the differentiators between high-octane gasoline and similar processes (e.g., methanol to gasoline), as well as key process metrics, such as carbon efficiency, CapEx, and product yield distribution. Additional project metrics could also include meeting frequency, publication count, and catalyst formulations. The interlaboratory project team appears to be working well together. The various roles of the project team members are not clearly outlined in a management plan. None of the project risks and mitigation strategies were mentioned. The key end-of-project milestones and targets were provided on the quad chart—namely, to demonstrate 200 hours TOS with 14% relative improvement in carbon efficiency for direct conversion of CO_2-rich syngas to high-octane gasoline in a single reactor. The improvement is assumed to be over the Fischer-Tropsch benchmark catalyst.

The communication plan for C1U was not explicitly stated. The project team mentioned being in constant contact with all principal investigators (PIs), as presented on slide 7. No industry advisors, subcontractors, or industry collaborators are involved in the work at this point.

The current approach in the C1U project of rationale catalyst design, characterization, and testing iterations is quite plausible and a widely accepted method for continuously improving the performance of new catalytic materials. The SOA for direct syngas conversion to fuels is Fischer-Tropsch. The block flow diagrams for the steps required in each C1U pathway should be clarified, as well as for the Fischer-Tropsch and MOGD baselines. The research approach of combining process and catalyst design iterations simultaneously has the potential to outperform Fischer-Tropsch fuel quality if high-octane gasoline types of product distributions can be obtained from the single-step pathway. The BETO Strategic Analysis Goals to develop commercially viable bioenergy and bioproduct technologies to enable sustainable, nationwide production of biofuels are supported with the C1U project, as are the Strategic Analysis Goals to ensure high-quality, consistent, reproducible, peer-reviewed analyses. The C1U project supports the Conversion R&D SMART Goal by 2021, completing the R&D necessary to set the stage for a 2022 verification that produces both fuels and high-value chemicals to enable a biorefinery to achieve a positive return on investment. The creation of a single-step syngas conversion catalyst that can also convert CO_2, compete on cost against Fischer-Tropsch materials, and create high-quality fuels is innovative. High-octane gasoline technology was recently licensed by an energy company, so the project team understands the importance of renewable high-octane gasoline fuels in the future that can be transported by pipeline. The impact of the distillate products on the industry was presented strongly. In many ways, this may be the more successful route, given some positive outlook forecasts for distillate demand strengthening. The Enerkem work was a huge impact and matches the desire of the BETO leaders to go into sustainable jet fuel. The project team has already shown commercial potential for the high-octane gasoline process technology. The C1U project was able to make notable progress toward the goal to develop renewable C1 conversion to flexible-fuels process technology with improved performance over the MOGD process baseline. The Cu/BEA catalyst was shown to be a superior catalyst relative to BEA alone. C4 recycle optimization was achieved to reduce the MFSP. It was unclear how the regenerative procedure changed due to knowing the absence of surface peptide nucleic acids It seems like the regeneration protocol may have a temperature change, saving only some utility expenses. A critical result was the C13 results proving that CO_2 activation occurred over CZA:Cu/BEA. The rational catalyst design iteration approach should be highlighted here to show how the formulation was determined in the project objectives. The use of stacked-bed configurations with methanol synthesis and high-octane gasoline catalysts to achieve direct syngas conversion to hydrocarbons was a positive result in pursuit of improved performance over the baseline. The use of nanoscale molybdenum carbide structures for olefin conversions appears to be a promising direction, as well as in direct CO_2/H_2 conversions. They did not see any performance hysteresis across regeneration cycles and the huge temperatures required to regenerate the material without copper. One of the challenges in the work is working at such low conversions and not providing a clear reaction pathway insight. The key end-of-project milestones and targets as provided on the quad chart were not achieved—namely, to demonstrate 200 hours TOS with 14% relative improvement in carbon efficiency for direct conversion of CO_2-rich syngas to high-octane gasoline in a single reactor. There was good progress made in FY 2020 on the single-step conversion. The risk mitigation plan for the single-step conversion not reaching this milestone was not provided. The project may have an opportunity to generate aviation fuel or racing fuel.

- This project is developing catalysts that enable the conversion of C1 intermediates to fuels and other high-value products. The project has clear management, including the risk mitigation strategy. The team collaborated with several enabling groups to help their catalyst preparation and conduct research to understand and design their catalysts computationally. The project has shown impressive advancement in fundamental research, demonstrating this by publishing in prestigious scientific journals. They possess two unique catalysts: one is nanoporous materials, and the other is nanoparticles. The unique chemical and physical features of these two catalysts provide a design space that could help achieve the mission of the catalytic upgrading program. It could be beneficial if the team could collaborate with CCPC and other enabling groups to investigate the confinement effect for their Cu/BEA catalysts and the nanoscale effect of their nanoparticle catalysts.

- This project seeks to enable conversion of C1 species to fuels and/or chemicals. A focus on aviation fuels and high-octane gasoline is appropriate due to anticipated growth in these sectors. The team is attempting to directly convert CO_2-rich syngas to fuels, which is a challenging and impactful target. They have already made headway in this respect, and continuing efforts will need to address high CapEx and limited product quality by intensification and operating at milder conditions.

  Management: The management structure is clearly outlined, including interactions with enabling platforms and TEA, as well as other consortia focusing on scale-up, process integration, and engine performance (Co-Optimization of Fuels & Engines [Co-Optima]). There is a clear communication structure with technical POCs identified for various enabling platforms.

  Approach: The team has outlined a vision for a dual research cycle that leverages foundational science and applied outcomes to target the major cost drivers of the process. This was a nice illustration of how one can feed from process-scale efforts in TEA, scale-up, and integration back to informed catalyst design and synthesis. At a conceptual level, this is a solid approach, and it is clearly benefitting a rational approach toward making the upgrading of C1 intermediates economically viable. From a technical perspective, this project aims to reduce costs for methanol-to-gasoline via process intensification and co-conversion of CO_2. Importantly, the team has identified that methanol synthesis and the downstream conversion of methanol to high-octane gasoline have compatible process conditions, providing an opportunity for intensification. In this space, the challenges and rationale for how to address them are clearly defined.

  Impact: Producing high-octane gasoline is a good near-term opportunity because it is a valuable relative baseline gasoline and it has increasing demand. The team has demonstrated the production of high-octane gasoline at the pilot scale with an industry partner, suggesting a scalable technology. The team has also demonstrated that they can upgrade olefins using mature oligomerization strategies to give mixed branched hydrocarbons with properties that match those of jet fuel. In this sense, the C1 platform enables the production of high-octane gasoline and jet fuel. It is noteworthy that the team has devised a system that converts methanol to triptane in excess of 70% selectivity. This was surprising to me considering the conventional “hydrocarbon pool” vision of methanol-to-hydrocarbons.

  Progress: The team demonstrated good yields of high-octane gasoline from DME. They are shifting toward direct syngas to high-octane gasoline, an appropriate next step in process intensification. The team has identified a BEA catalyst that is selective to branched alkanes, whereas a conventional MFI usually produces aromatics. I noticed that the team quantified the cost of catalytic upgrading in isolation as opposed to assessing the total dollars per GGE of the technology. I prefer this because it de-emphasizes things like coproducts from lignin, which are out of scope for ChemCatBio programs, and it places the focus solely on the impact of catalysis research. I like the use of ultraviolet-visible for *in situ* characterization. Identifying polycyclic aromatics is important to understanding the stability of Cu/BEA, and insights about their formation led to improved regeneration protocols. With respect to intensification, compatible operating conditions in methanol synthesis and upgrading hint at the ability to integrate the two processes in a single reactor but guarantee no such thing. It is noteworthy, then, that the team has demonstrated the ability to directly convert CO_2-rich syngas with catalysts developed here. At a fundamental level, CO_2 co-feeding experiments are informative as to the fate of the CO_2 co-feed. Isotopic labels clearly show the direct incorporation of CO_2 into products, which is significant.

PI RESPONSE TO REVIEWER COMMENTS

- We appreciate the positive comments from the reviewers highlighting our innovation over Fischer-Tropsch; our approach to use process intensification for a single-step syngas-to-fuels process; our ability to generate distillate fuels; and our notable progress to date, including isotopic labelling studies showing the incorporation of CO_2 into the hydrocarbon products. To reiterate our carbon-efficiency goal, we seek to improve the carbon efficiency of the process by 14% relative to the previous three-step process we were developing through the use of process intensification. The overall carbon-efficiency goal of 32% would meet that of the benchmark MOGD process when employing a biomass feedstock. With respect to the regeneration protocol that was recently developed for the Cu/BEA catalyst, we believe that the cost savings goes beyond utility expenses. We recently reported that the catalyst lifetime can have a 3%–5% impact on the overall MFSP, depending on the regenerability of the catalyst, where a catalyst that can be efficiently regenerated for 5 years can reduce the MFSP by 3%. Considering an MFSP of $3/GGE, this is $0.09 per gallon of fuel. We appreciate the comments about the challenge of obtaining insight into the reaction pathway in our single-step conversion of syngas to hydrocarbons, especially with Cu-Zn catalysts that the reviewers are correct to identify as good water-gas shift catalysts, and the related comments about partnering with the CCPC and other enabling technologies. Toward this end, we have already begun a collaboration with the CCPC to model the series of reactions that occur in our process intensification, single-reactor approach. This collaboration will provide insight into the chemistry by understanding the equilibrium limitations of each reaction. Further, this effort will aid reactor design to maximize per-pass hydrocarbon yield and understand how to best recycle byproducts, such as CO_2 and isobutane. As an example of collaboration, our experimental project team will inform the computational model using results from CO_2 co-feed experiments designed to simulate CO_2 recycle in the system to understand equilibrium limitations.

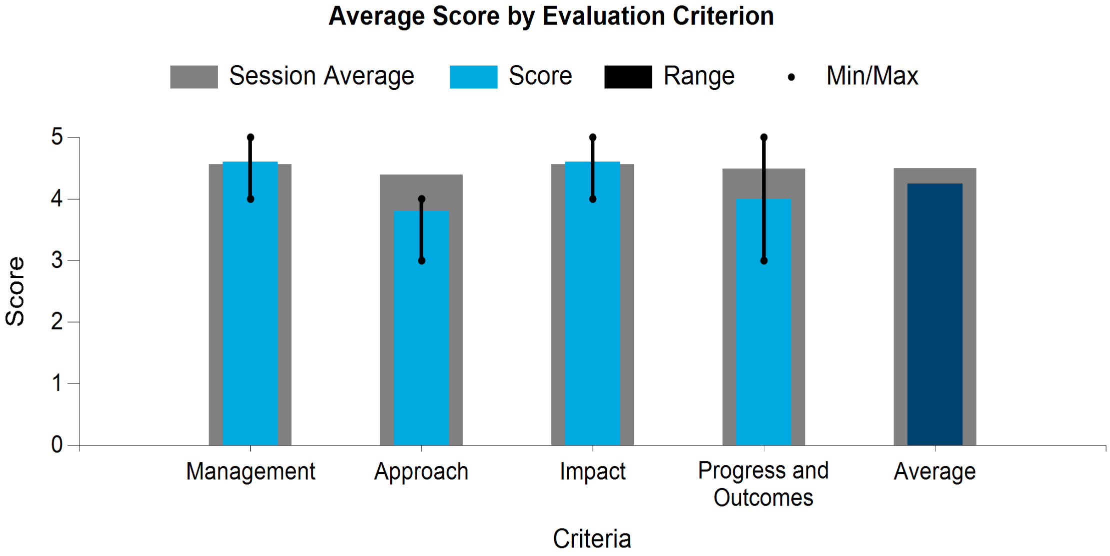
CATALYTIC UPGRADING OF PYROLYSIS PRODUCTS

National Renewable Energy Laboratory

PROJECT DESCRIPTION

WBS:	2.3.1.314
Presenter(s):	Adam Bratis; Mike Griffin; Zia Abdullah
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2022
Total DOE Funding:	$6,800,000

CFP is a versatile pathway for the direct liquefaction of biomass and waste carbon sources to generate a stabilized bio-oil intermediate that can be further processed into renewable fuels, chemicals, and materials. The objective of this project is to advance the CFP SOT through integrated catalyst and process development, expand market responsiveness by creating routes to novel coproducts, and provide experimental data to inform process modeling and scale-up activities. Research advancements during the past 2 years include reducing analytical uncertainty by achieving 100% ± 1% carbon balances during reaction testing with woody biomass, improving process efficiency by achieving a four-time increase in catalyst cycle length, demonstrating compatibility with waste feedstocks, and confirming process durability for 100+ reaction cycles. Additionally, this project supported a comprehensive pathway review to evaluate scale-up needs. This review resulted in the early identification of technical risks and informed proactive planning for the BETO 2022 verification. Other impacts from this project include the generation of broadly enabling scientific knowledge (14 publications and 18 presentations since 2019), engagement with industry partners (e.g., Johnson Matthey and ExxonMobil), and the identification of a promising pathway to market that addresses emerging demands for biogenic refinery feedstocks.



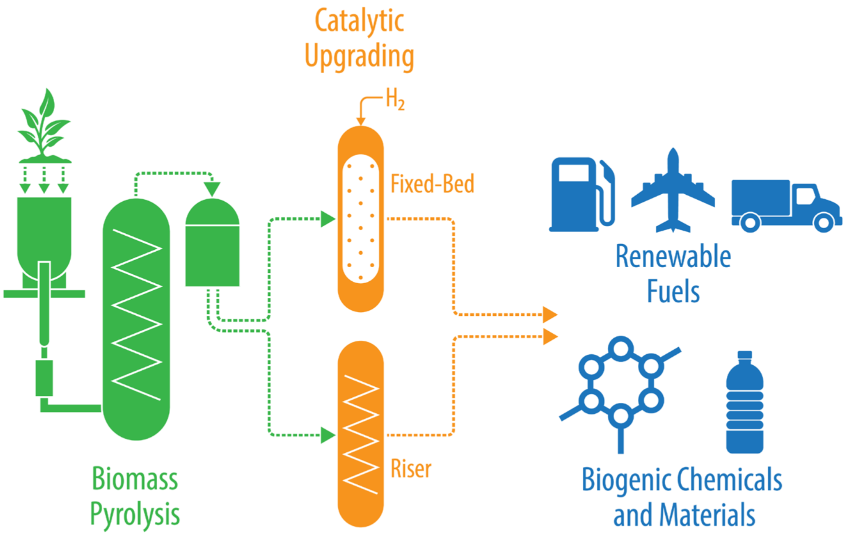


Photo courtesy of NREL

COMMENTS

- The management team is well organized and integrated within the government laboratories. The partnerships via cooperative research and development agreements (CRADAs) with external fuel and catalyst companies is an important aspect of the program. Team integration and communications had a large impact on speed and results. Cross integration of all aspects—from modeling, feedstock, and catalyst development—and refinery integration as parts of the plan allowed for fast progress in the program toward the milestone of $3/GGE. The team's approach of using CFP to stabilize the bio-oil is the right way forward in my opinion. There is no major issue with impact because the program could be a good fit with existing refineries (to be proven) and has the potential to meet the $3/GGE target unless it is too dependent on coproduct end use, which was unclear in the presentation. Achieving 100% carbon balance was an important milestone, along with the TOS. My only concerns are temperature for the catalytic process and Pt cost on a large scale. Although the Pt system is the best, the supply shortage in the industry may cause issues in commercialization; thus, I would like to see in the review how their current result for catalyst loading compares to the current Pt/TiO_2 catalyst used. The current supply of Pt is constrained to approximately 7–8 million oz per year. Is there any concern by the team around longer-term implications of the circulating sand system for potential reactor metal erosion and the particle size degradation of sand? Is there a reason why no GGE is shown at this stage for the project as it moves toward scale-up?

- The CFP project is developing catalysts and processes for the direct liquefaction of biomass. They build active management that benefits their research. This project is showing significant advancement in the efficiency of their catalysts and the overall process. The progress of this project helps achieve the mission of the catalytic upgrading program. It is also impressive that the team is working with the enabling groups to investigate the deactivation of the catalysts. The durability and regeneration of catalysts could change the game for the pyrolysis of biomass, considering the contaminants inside. It could be beneficial if the team could enhance their collaboration with the other enabling groups, including CCPC and catalysis synthesis, to conduct foundational research on the fundamental relationship between the catalytic ability and the surface pattern of the Pt/TiO_2 catalysts. This relationship could help determine the strategy to improve catalysts. In addition, it is interesting to see their research on the deactivation of catalysts using forest waste as the feedstock. Their research outcome reminds us of the importance of feedstock quality on performance, especially the durability of the catalysts. It is very expensive to have a highly purified biomass feedstock. This research could be used as the starting point for the study of developing catalysts and processes that can handle the “low-quality” biomass.

- The distribution of tasks to individuals helps provide individual accountability. Coordination among these can be challenging, but it appears to be smooth in this project. Did the discovery of the “lost carbon” change your view of the most attractive of the three process options? Have you tried simply recycling the oxygenates to the first step? Is your pyrolysis oil suitable for a refinery feed to fluid catalytic cracking (FCC) or hydrotreater? Potassium hydroxide is transported with the gases to the deoxygenation. Can it be removed, for example, by a solid acid guard bed? Have you tried a simple water washing that removes most of the K? Another option is to use K-free cellulose or lignin or both. This process seems to be a variant of the KiOR process. Do you have access to their data? Would it be useful? It seems like this project missed opportunities to demonstrate viability. Although I am not convinced that catalytic pyrolysis is not viable, a pivot to coprocessing in FCC or hydrotreater is a good direction that is attractive for refiners.

- The key goals and objectives of the project are presented on slide 4 and on the quad chart (slide 22) to develop CFP technology with the flexibility to produce specific types of bio-oils in support of the BETO 2022 verification targets. There was no mention of quantitative technology development targets, KPIs, or improvements to guide the pursuit of the project goal. The 2018 baseline, mentioned on slide 9, provides some idea of a technology trajectory and process KPIs focused on carbon efficiency and oxygen content. The management plan was clearly outlined on slide 5, with the critical work breakdown specified with project leads and role assignments for each element. This appears to be an effective team organization style that is further strengthened by a dedicated project management role in Task 1. None of the project mitigation strategies were mentioned for the key risks discussed on slide 19: feedstock quality risks, catalysts durability risks, process integration risks, and TOS risks. The key end-of-project milestone provided on the quad chart was to develop pathways that could be integrated within the traditional refinery and provide the quality specifications for corresponding product streams. The criteria for a developed technology pathway are defined by the 2022 verification goals. The team has a stage-gate-type risk mitigation management approach. The communication plan for the project was not explicitly stated. It was mentioned that the team meets about three times per month. There is quite a bit of cross-laboratory knowledge sharing. The project team is highly collaborative across ChemCatBio, including key CRADAs with a catalyst manufacturer and major energy company. The team leverages the ChemCatBio IAB. At this point in the project, the approach will lead to a new innovation in catalytic upgrading process catalytic material design and performance, especially in the areas of lifetime, stability, and turnover. The best cost-competitive process configuration has already been set. Most of the work centers around parametric operating optimization with new catalyst formulations, which does not require a focus on step-change innovation to reach the 2022 verification objectives. Real process problems must be defined well and solved methodically. More discussions around the real problems, risks, and threats facing the 2022 go/no-go decision point would be useful. The project team realizes that they have a unique opportunity to supplement the fats, oils, and grease market with the bio-oil products resulting from this technology. More comments about co-feeding with fats, oils, and grease were expected because this is a timely discussion. The project has resulted in numerous publications and spin-out projects. The two CRADAs established prove that this technology has commercial potential, especially in the area of coprocessing. Toward the goal of developing CFP technology, the team has made helpful progress during the last few years in the areas of analytics, pyrolysis cycle durability, and fixed-bed TOS. The current catalyst lifetime, even though it is an improvement, continues to be an issue, even if several banks in switching mode are implemented in the commercial design. There are many objectives to be accomplished to reach the goal of developing CFP technology fully. The team has made good progress toward the original goals. The key end-of-project milestone to develop pathways that could be integrated within the traditional refinery and provide the quality specifications for corresponding product streams was partially reached, as specified on slide 13, where the team was able to supply bio-oil to several BETO projects. The quality specifications for various bio-oils have not been established yet. The no-go decision was based on the schedule and not on any major technical issues. It does not mean that this technology was not viable.

- This project is focused on upgrading pyrolysis vapors in order to efficiently convert low-value bio-oil into fungible fuels. CFP is an important part of the biomass upgrading portfolio because it is feedstock-flexible and can produce a bio-oil from most carbon-based resources. The long-standing challenge is in converting that bio-oil to useable fuels or chemical products at an economically viable cost. The research effort of this program is appropriately directed mainly toward bio-oil upgrading.

  Management: The management structure, including individual task leads, is clearly identified, with an appropriate communication strategy. The management team has identified and continues to identify risks, and they outline appropriate mitigation strategies. There is a strong connection between the CFP program, enabling projects (TEA, ACSC, etc.), the CCPC, the feedstock consortium, the IAB, and industry partners. The multi-lab organizational structure with identified POCs at each are clearly identified. This hierarchy is sensible and well thought out. There are no significant weaknesses in the management of this project.

  Approach: The presentation highlighted a comparison of *in situ* CFP and various *ex situ* methods, ultimately finding that *ex situ* hydrotreating bio-oils in a packed bed was the most carbon-efficient. Research in this space led to the identification of a low-loading Pt/TiO_2 catalyst, which is effective for bio-oil upgrading. Importantly, the team relies on strong electrostatic adsorption to increase and stabilize Pt dispersion, making this formulation far more economic than previous generations of upgrading catalysts. Research has been aimed at reducing risk and diversifying feedstocks, which are appropriate directions. The team identified an increase in MFSP and found that simultaneous scale-up and process refinement would be necessary to meet MFSP targets in 2022, so it has pivoted to a strategy of providing stabilized bio-oils as a direct input to refinery hydrotreaters. This is a reasonable direction for near-term economic viability.

  Impact: The shift in scope allows the team to potentially provide biogenic inputs to refineries for the production of fuels and chemicals, which is increasingly in demand. The team has been active in publishing and presentations, they have an impressive intellectual property portfolio, they have created partnerships with industry, and they have created multiple spin-offs that leverage technology from CFP program.

  Progress and outcomes: The team is commended for improving analytics to close carbon balances. Bio-oils and their derivatives are poorly characterized, so better analytical methods is a significant advance for the field. Although this led to a pivot away from stand-alone hydrotreating, it is an important outcome for pyrolysis research, and the work also identified a potential revenue stream of oxygenated coproducts. The team has made considerable progress in scaling and improving catalyst activity and durability. They have generated 10 L of (treated?) bio-oil, impacting programs throughout BETO. They have also shown that smaller TiO_2 particles improve both activity and on-stream stability, a significant outcome for a bio-oil hydrotreater. Finally, the work on demonstrating feedstock flexibility using mixed forest residues instead of relatively clean model feeds is extremely important because full-scale processes will necessarily use lower-grade feedstocks. This project has built foundational knowledge in catalysis. One of the most important outcomes is the description of potassium-induced deactivation. This was a good demonstration of the impact of interfaces with enabling programs in ACSC, CCPC, and CDM. Data have enabled the development of finite element method models that are able to build heat and mass transfer into full-scale CFP reactor models. The project will result in a technology report, which will be a great benefit to the field.

PI RESPONSE TO REVIEWER COMMENTS

- We thank the reviewers for their excellent feedback, and we appreciate the positive comments related to our project's management structure, approach, progress, and impact. As highlighted by the reviewers, the successes of this project have resulted in notable advancements in both foundational science and applied engineering, which have translated into significant improvements to the SOT for CFP. These advancements have been a result of a coordinated research effort spanning multiple laboratories and consortia, and we would like to acknowledge our many collaborators for their contributions. We also agree that additional research is needed in this technology area. In that context, we offer the following responses to clarify certain elements of our research approach and summarize our plan moving forward:

    - The Pt/TiO_2 catalyst was downselected due to its ability to promote deoxygenation while maintaining comparatively high carbon yields relative to all other catalysts evaluated, and we agree that catalyst cost and Pt availability are important factors in the overall process economics and viability. To help mitigate these issues, past research in this project has focused on adapting synthesis techniques to enable a reduction in Pt loading from 2.0 wt % to 0.5 wt %, which translated to a decrease in material cost from $805/kg to $204/kg, as estimated utilizing the ChemCatBio CatCost™ tool. Moving forward, our team is also developing catalysts that do not contain noble metals (e.g., Mo_2C, material cost $62/kg). We have demonstrated the ability of these lower-cost materials to effectively upgrade pyrolysis vapors, and ongoing research is focused on developing regeneration procedures for this promising class of catalyst.

    - We agree that carbon intensity is a critical metric for assessing technology pathways. Based on the most recent SOT report, the NREL *ex situ* CFP process achieves an 83% reduction in greenhouse gas emissions compared to fossil-based pathways. Additional information, including comparisons to other pathways, can be found in a publicly available report at OSTI.gov titled *Supply Chain Sustainable Analysis of Renewable Hydrocarbon Fuels via Indirect Liquefaction, Ex Situ Catalytic Fast Pyrolysis, Hydrothermal Liquefaction, Combined Algal Processing, and Biochemical Conversion: Update of the 2019 State of Technology Cases*. Technical progress toward other quantitative targets (e.g., process carbon yield, bio-oil oxygen content, MFSP) are summarized in annual reports that are also available at OSTI.gov.

    - As the reviewers correctly point out, durability is an important issue for all biomass conversion pathways. Through research in this project, we have demonstrated stable performance over 250 hours TOS using clean pine feedstocks. We have also worked collaboratively with the ChemCatBio enabling projects to provide foundational, atomic-level insight into potential deactivation mechanisms associated with inorganic compounds found in lower-cost forest residue feedstocks. Through this collaborative research, we have identified promising mitigation strategies, including the use of inexpensive guard beds and water washing. Further research in this important area is a priority for ongoing experimental campaigns, and updated data will be included in an end-of-year report.

    - We agree with the reviewers that there is an opportunity for this project to address a near-term demand for biogenic refinery feedstocks, and we intend to build upon our existing research to produce high-quality bio-oils tailored for refinery coprocessing. Within this scope, an important goal will be catalyst and process development to create routes for the conversion of lignocellulosic feedstocks to renewable diesel and sustainable aviation fuels. As part of this effort, we will apply our comprehensive analytical capabilities to clearly establish bio-oil quality specifications for refinery insertion points of interest and leverage our existing partnerships and collaborations to drive research to commercially impactful outcomes.

CONDENSED PHASE CATALYSIS TECHNOLOGY FOR FUELS AND CARBON PRODUCTS

University of Tennessee

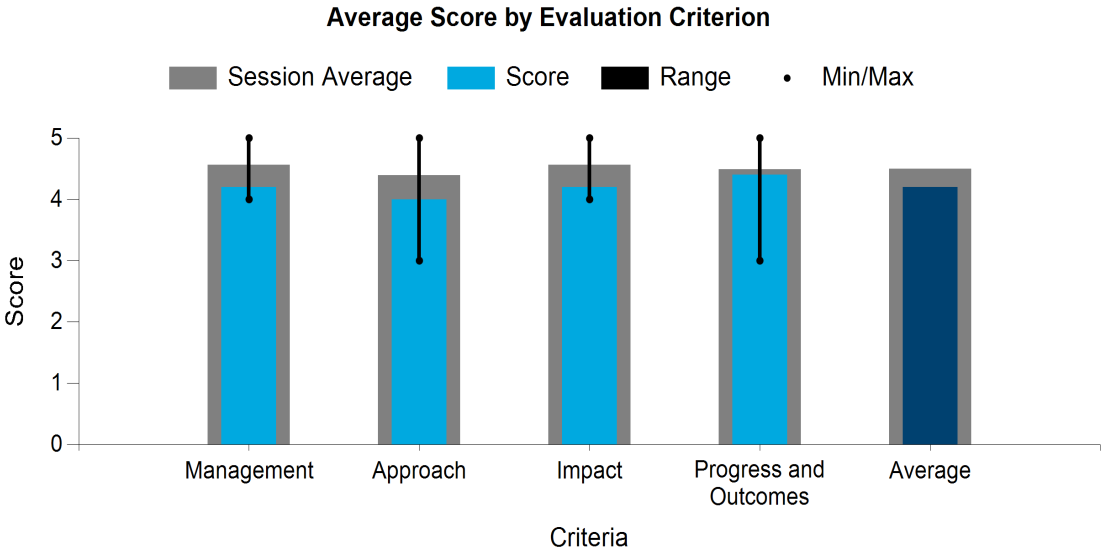
PROJECT DESCRIPTION

WBS:	2.3.1.413
Presenter(s):	David Harper
Project Start Date:	08/01/2018
Planned Project End Date:	03/31/2021
Total DOE Funding:	$1,400,000

The project’s main objective is to maximize biomass use to simultaneously produce fuels, chemicals, and materials. The goal is to separate biomass into high-purity streams of its three main components—cellulose, hemicellulose, and lignin—in an integrated process. This enables great flexibility in the fuels and chemicals produced and supports combining our technology with other downstream conversion processes. Our gamma-valerolactone (GVL)-based biomass conversion platform enables a true biorefining capability that shares traits with petroleum refining. In brief, a variety of biomass types (including mixes) are deconstructed and fractionated into intermediates that are further refined into products. Converting the entire “biomass barrel” to products decreases unit production costs by allocating fixed and variable costs across an increased product volume. Because the economics to produce fuels are so challenging, valorizing all the biomass is essential. We converted the biomass into activated carbon products (from lignin), furfural (from hemicellulose), and fuels (from cellulose and hemicellulose). According to this objective, we have accomplished the following:

1. Used a biomass-derived solvent GVL to fractionate multiple bioenergy crops to produce high-purity fractions (>90%) of cellulose, hemicellulose, and native lignin at low cost and high concentration (>20% biomass).
2. Produced high-value activated carbon products from unique, high-purity, GVL-derived lignin that reduces the cost of the biofuels.
3. Established an intermediate chemical from the hemicellulose (furfural) to reduce the cost of cellulosic ethanol <$3 GGE using established models.
4. Converted hemicellulose and cellulose to aviation fuel (alkenes) via intermediate chemicals derived from biomass polysaccharides (i.e., furfural, levulinic acid).
5. Demonstrated the techno-economic viability of the integrated processes.

We obtained the necessary basic knowledge and validation to start more detailed engineering work to attract funding for a pilot- and demonstration-scale project. Our previous work has proven the performance of our process at the laboratory scale for each component (TRL 3). Our integrated processes demonstrated realistic conditions (TRL 5) necessary for scaling up.



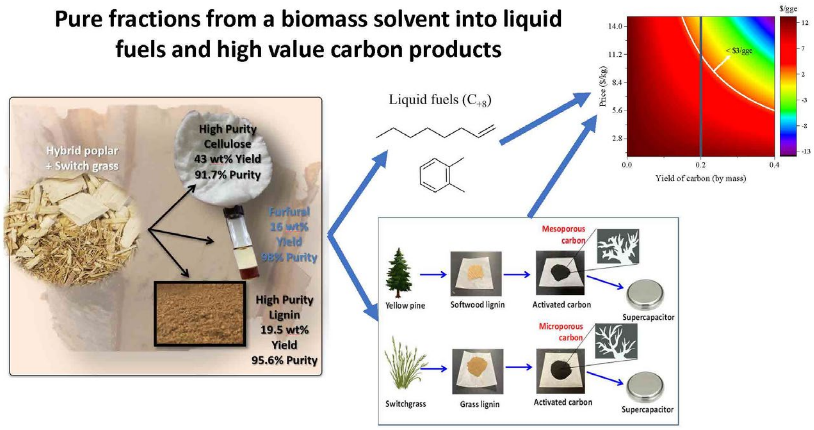


Photo courtesy of University of Tennessee

COMMENTS

- All elements are managed well, as multiple aspects had to come together to meet success. This seems to be the smart approach, as direct biomass conversion as a whole is challenging to get economics on par with petroleum fuels and much value-added mass is lost in the direct conversion. The impact could be substantial based on the economic analysis to date and the fact that the teams can obtain clean materials for further conversion. The solvent cost and recycle recovery are key to impact. There are no major issues with their progress and outcomes. The team has made excellent progress on the original goals to provide separated feedstocks at high quality. The fact that the solvent is sourced from the biomass and shown to recycle with good recovery is solid and is a key result the team has achieved. Also interesting is the lighter color of the lignin versus typical lignin recovered from other commercial processes practiced currently. Poplar lignin is one source that provides low color. Was this biomass from poplar?

- The separation of lignin, cellulose, and hemicellulose is practiced widely with known technology. It is not clear that the GVL extraction produces better yields or purities of these materials; where is the advantage? The high-surface-area lignin (4,497 m^2/g) could be very useful as a precursor to activated carbon, a biocarbon, or as a filtration material. Are you looking into the conversion of the lignin to activated carbons? The production of a high-value activated carbon seems to be the most attractive path for this technology to be commercially viable. That may not interest GlucanBio, but others may be interested.

- The key goals of this project are presented on slide 2 and the quad chart (slide 29) to separate biomass into high-purity streams of cellulose, hemicellulose, and lignin that enable easy conversion to hydrocarbon fuels (meeting the $3/GGE target), high-value carbon products, and chemicals. The KPI associated with the goals are >20% co-biomass, >90% C5 deconstruction stream, >90% C6 deconstruction stream, >95% lignin deconstruction stream, >98% pure furfural, >96% pure cellulose, and >98% pure lignin. The tasks and roles are divided and clearly assigned between the University of Tennessee and the University of Wisconsin, with Task 2 belonging to GlucanBio. The risks were not identified along with the mitigation actions. The KPIs mentioned can be regarded as milestones because no intermediate targets were provided. The communication between teams was not clarified, as well as the engagement with the industry partner, GlucanBio. The project has no apparent IAB interactions to deal with the chemical product considerations. The year-two process configuration approach, having the GVL produced internally to the process and focusing on very narrow distributed saturated butene trimers into the jet fuel market as C12, seems more attractive. Further, the specialized carbon precursor materials could advance the SOA in the anode market. The SOA to compare this work is not obvious. There was definitely advancement from the original conceptual design proposed the first year of the project. The work supports the BETO and technology area mission of developing and demonstrating transformative and revolutionary bioenergy technologies for a sustainable nation, as well as the BETO goals to develop commercially viable bioenergy and bioproduct technologies. The project supports the Conversion R&D SMART Goal for 2021, completing the R&D necessary to set the stage for a 2022 verification that produces both fuels and high-value chemicals to enable a biorefinery to achieve a positive return on investment. The project addresses several key barriers in Synthesis and Upgrading—Ct-H. Efficient Catalytic Upgrading of Sugars/Aromatics, Gaseous and Bio-Oil Intermediates to Fuels and Chemicals and Integration and Intensification Challenges. The approach of generating pure streams to make high-quality fuel and chemical products has been a cornerstone processing philosophy for decades within the chemical and hydrocarbon processing industries, so there is not much innovation from the design premise standpoint. When finally applied, a narrowly distributed alkane jet stream could be innovative and even command more of a premium than currently exists. The amount of unit operations in the process continues to make this process unattractive from a complexity index standpoint. The GVL solution was a great example of how to continue to intensify the operations. The team appears to understand the impact of their project work on the scalable needs of the bioenergy community, as well as the goals and challenges cited by BETO in the Multi-Year Program Plan, particularly in the area of lignin valorization and chemical production. This project definitely has commercial potential outside of only working with GlucanBio. There are no clear industry engagement or ties mentioned in the work to show interest. The project was able to accomplish the goal of separating several pure streams on schedule. The team was able to show cycle recovery of the GVL solvent in the fractionation work where all the milestones were met. The activated carbon work was impressive, with 4,500-m^2/g surface area materials produced in one step from readily available lignin derived from kraft pulping commercial operations. It is important to keep optimizing the GVL-based systems for high-surface-area carbon production. Space velocities for GVL conversion and oligomerization are quite low. The team should report the net present value metric for such an intensive CapEx. The role of supercapacitor carbon was quite important to swing the economics positive. The mild coking and deactivation on ZSM-5 when passing butenes should be discussed as well. The team should investigate doing a TEA based on a process flow diagram instead of a block flow diagram, allowing for the next level of processing detail to enter the discussion. All of the milestones have been reached. The risk mitigation plan for GVL-activated carbon optimization was not discussed because there were no quantitative targets established in the beginning of the project concerning this coproduct quality.

- The overarching goal of this project is to fractionate biomass into high-purity streams to enable cost-effective selective upgrading. The project will use a biomass-derived solvent (GVL) to enable fractionation. Fractions are converted into furfural, cellulose (and derivatives like levulinic acid, GVL, and aviation fuels), and lignin-based carbon products. The target goal is $3/GGE fuels. The carbon products and furfuryl alcohol are interesting and high value, but it is unclear if their market volumes are commensurate with aviation fuels. Their near-term impact as a coproduct may be limited, but there is certainly considerable long-term potential.

  Management: The management strategy is clearly outlined, with task leaders appropriately designated based on expertise. These cover all the bases of a biorefining process, including feedstock selection and analysis, fractionation, upgrading, product testing, and TEA.

  Approach: The technical approach is based on using valerolactone solvent to aid in the fractionation and upgrading of biomass. The team has considered the impact of feedstock variability using three feedstocks in isolation and in combination—switchgrass, poplar, and yellow pine—all of which are relevant. The overall goal is to maximize biomass loading, minimize degradation in conversion steps, minimize separation burdens, and recycle the valerolactone solvent. There is a clear identification of potential challenges and risks, as well as potential resolutions. The team is producing furfural (and derivatives) from C5 sugars, levulinic acid (and derivatives) from the C6 fraction, and carbon products from lignin. The team is leveraging high-value coproducts to decrease the MFSP of fuels. The project has a stated focus on stability during integration, which is presumably associated with impurity carryover. This is an important aspect to consider in an integrated process.

  Impact: This process has demonstrated the ability to handle high biomass loadings and operate at mild conditions. The former, in particular, is critically important to production cost, so maximizing solids loading is an important impact. The solvent employed is bio-derived, nontoxic, and recyclable. The team has also demonstrated that their fractionation and upgrading strategy is effective at converting 80% of input biomass into various products at their stated purity specification. Efficacy demonstrations for integrated processes are still lacking in the biomass processing field, so this is an important impact.

  Progress and outcomes: The team has made considerable progress in integrating and scaling this solvent-based fractionation strategy for selective biomass upgrading, achieving specific milestones during the project. The conversion of lignin into carbon-based products is welcome considering the impact that lignin valorization has on the MFSP of advanced biofuels. In this area, the team has demonstrated the production of battery-grade graphite and carbon quantum dots, which are both high value. There has been considerable effort at integrating the various steps in this process, which is critically important in a cascade like this because it reveals the degree of purification required between each unit operation. Overall, the technology seems relatively robust. Furfuryl alcohol and lignin-based carbons are both probably viable commercial products now. GVL to jet fuel may not be entirely cost-effective yet, but with the forecast demand for aviation fuel, having a biogenic route is attractive, nonetheless. The group has achieved the project target of producing liquid alkenes below $3/GGE.

- This project aims to develop an integrated process that can separate biomass into high-purity streams of its three main components: cellulose, hemicellulose, and lignin. Achieving the project goal could help develop more comprehensive processes that produce high-quality feedstocks, which is critical for catalysis. The team is managed properly and has shown the success of achieving their goal. The utilization of a bio-based solvent seems to be interesting, and it would be beneficial if we could better understand mechanisms and design more solvents that can benefit from the reactions or separations. Similar bio-based solvents could be high-value coproducts too.

PI RESPONSE TO REVIEWER COMMENTS

- Yes, the hardwood feedstock was from a hybrid poplar (*Populus* spp.) grown specifically as a bioenergy feedstock. The material was harvested, cut, and debarked prior to size reduction at the University of Tennessee. The difference in color is most likely the low degree of oxidation and condensation compared to other processes, such as the kraft process.

- This is an excellent point. In our analysis, we are completely converting the lignin stream to supercapacitor carbon, resulting in the annual production of 47.3 kilotonnes; however, the total market of supercapacitor carbon in 2019 was 218 kilotonnes, which is expected to increase fivefold by 2027 (assuming the price to be $15/kg). Still, a single biorefinery supplying 22% of the total supercapacitor carbon production may be too risky. Further, the energy requirements of the process are met by combusting natural gas, making the biorefinery net carbon positive. We recognize that careful analysis is needed regarding splitting the lignin stream so that a portion of the stream is used to produce a variety of carbon products (e.g., quantum dots, supercapacitor carbon, filtration material), and the other portion is used to satisfy part of the energy requirements to balance the economic and environmental trade-offs. Nevertheless, our analyses suggest that valorizing lignin to produce carbon products can enable biorefineries to achieve a higher return on investment. The amount of unit operations in the process continues to make this process unattractive from a complexity index standpoint. The GVL solution was a great example of how to continue to intensify the operations. The process flow diagram still shows many unit operations, but almost all the separation/purification steps have been removed. Even though each catalytic reaction has been separated in the process flow diagram for clarification, many of those can be (and have been) integrated already. For example, the hydrogenation of furfural to furfuryl alcohol, the conversion of furfuryl alcohol into levulinic acid, and the hydrogenation of levulinic acid are three blocks, but they can be performed in a single reactor with three catalytic beds and three temperature sections. The conversion of GVL to alkenes is also integrated.

- Professor Dumesic and other groups are studying the mechanism and exploring other similar solvents, but that work is out of the scope of this project. In this project, GVL was chosen because it can be the solvent for all the reactions involved, and it is directly converted into the final products (butene and, finally, C8–C12 alkenes), eliminating the separation steps. The use of other solvents would be possible, but the intermediates/process diagram should be different to avoid the separation issues.

- Most of the processes proposed in the literature seem to be technically viable but not economic. The yields/purity reported typically exceed 90%, so there is no room for improvement there. The current project aimed to obtain a similar yield (near 90%) simultaneously for all three fractions. (Notice that from the same biomass, we produce cellulose, hemicellulose, and lignin at high purity and high yield. In other processes, only cellulose, hemicellulose, or lignin may be optimized to get one or two products at high yield, but they lose the value of the third.) And we are working at economically attractive conditions (i.e., high biomass loading, high biomass flexibility in terms of size and nature, minimal separation steps because the solvent is the final product, and solvent recovery and reutilization).

  The advantages of GVL as a solvent can be summarized as follows: (1) It works with a variety of biomass types and requires no biomass pretreatment (drying or size reduction beyond wood chips). (2) It works with a high biomass loading (~30 wt %). This significantly reduces equipment sizes, solvent losses, and downstream separation costs. (3) It has a high boiling point, which allows low-pressure digestion. This is critical to achieve high biomass loadings in a continuous process reactor and to minimize evaporative solvent losses. (4) The biomass deconstruction occurs at very mild process conditions, so the lignin produced has a less condensed structure, has high purity, and retains its value as a precursor for high-value polymer, carbon products, or aromatics. This is an economic game changer compared to burning lignin as fuel. (5) Post-digestion, clean cellulose, and hemicellulose fractions enable independent stream coprocessing under optimum conditions to maximize their product value. The cellulose has a very high purity and has utility for other conversion technologies. (6) To offset GVL losses, the process design makes GVL *in situ* as a process intermediate. This reduces and eliminates separation steps because biomass-upgrading reactions occur within the GVL. The GVL itself, one of the final intermediate products, is a suitable intermediate for liquid fuels, so the solvent recovery/separation is unnecessary. Eliminating separation steps improves the process economics, minimizes the solvent losses, and decreases/eliminates GVL purchasing costs. (7) It enhances acid-catalyzed dehydration and hydrolysis reactions, both critical to biomass conversion. (8) GVL or its derivatives do not react with biomass-derived products or impurities, such as what happens with other solvents like ethanol, glycerol, or tetrahydrofuran. This reduces the solvent losses. (9) It has a low heat of vaporization (25% that of water) to reduce energy costs. (10) It is safe, does not have a foul odor, and is a food additive when used in low concentrations.

We are continually working on process optimization for converting lignin into activated carbons. Some material characterization was not completed on time for this review for the produced activated carbons. We are in the process of applying them as the electrodes in supercapacitors and batteries for energy storage. Also, we are testing these carbons as adsorbent for methylene blue and heavy-metal removal. Even though it is beyond the scope of this project, softwood kraft displays promise as an absorbent for methyl mercury because the thiol groups are produced upon further reduction.

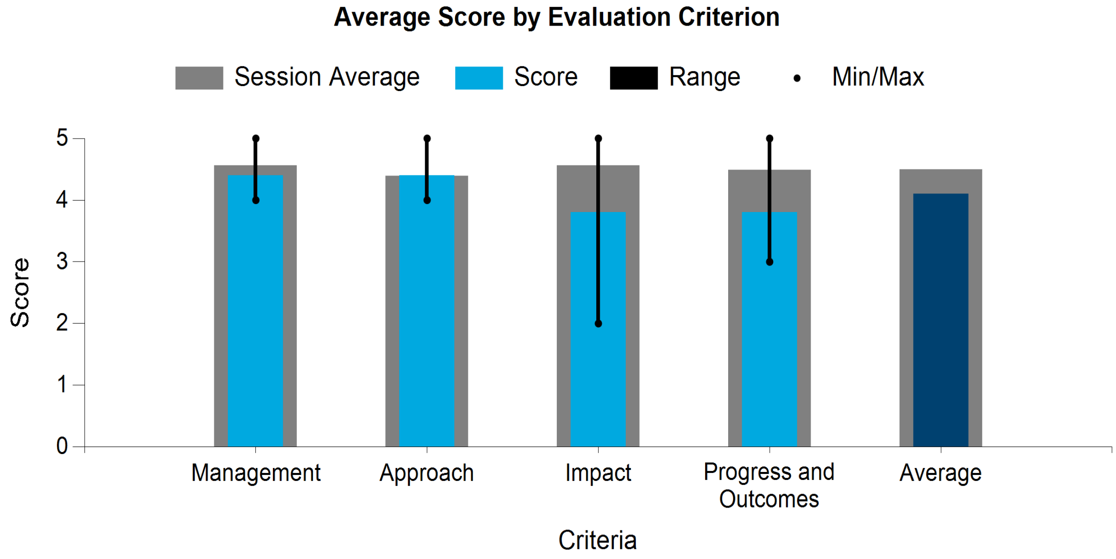
INTENSIFIED BIOGAS CONVERSION TO VALUE-ADDED FUELS AND CHEMICALS

University of South Florida

PROJECT DESCRIPTION

WBS:	2.3.1.414
Presenter(s):	John Kuhn
Project Start Date:	10/01/2018
Planned Project End Date:	09/30/2022
Total DOE Funding:	$1,836,459

The overarching goal of this project is to convert biogas obtained from landfills or anaerobic digesters to hydrocarbon fuels and chemicals. The specific goal is to develop an intensified process to reduce CapEx and enable a 15% reduction in MFSP relative to SOT. This project also aims to diversify products from biogas conversion and minimize flaring. The project management plan allows each organization to focus on its core capabilities to enable rapid catalyst and process development. The project leverages DOE resources, including ChemCatBio. The development is accelerated by an iterative, multifaceted approach to R&D challenges. Activities focus on critical success factors by addressing the go/no-go criteria and reducing project risks. The approach is to integrate catalysts tuned to specific reactions into the same reactor bed. The project, so far, has doubled the single-pass production non-methane hydrocarbon products compared to the SOT. Gains are obtained via catalyst development, concurrently to minimizing the use of precious metals and the tuning of conditions. It is anticipated that the inherently improved heat and mass transfer will reduce both costs and fossil fuel greenhouse gas emissions compared to alternatives. The project addresses several BETO barriers, such as increasing yields from catalytic processes, decreasing the time and cost to develop novel industrially relevant catalysts, and improving catalyst lifetime.



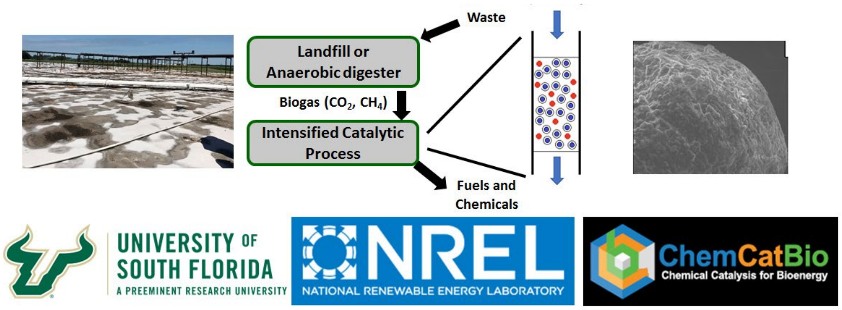


Photo courtesy of University of South Florida

COMMENTS

- The project management is solid, and no issue is seen. There is no issue with the approach because landfill gas is a significant issue for the environment, and better utilization of the gas for fuel implementation—although used to generate electricity today—has been scattered. It is difficult to see the impact being substantial, with low yields to date and the target for the end of the project of 10% at the bench scale. As with most processes, converting syngas and scaling up is the big challenge down the road, even if they can achieve their current target. Progress seems slow, and the outcome to have a major impact in the future seems challenging; however, there is some nice work overall on catalyst and process development.

- The goal is very attractive, and the approach of using the different capabilities seems appropriate. Is a 10% C2 yield an interim target? The process likely needs to achieve a much higher yield to be economically viable. What does "conventional" dry reforming and Fischer-Tropsch provide? The Fischer-Tropsch and steam methane reforming (SMR) reactions operate at very different conditions, as stated. Can CH_4 activation ever be fast enough to be used at Fischer-Tropsch temperatures? (I think not.) Would a layered SMR catalyst in the stacked-bed configuration be a better choice because the Fischer-Tropsch products would not see the SMR catalyst? The attention to small-scale applications is appropriate because landfill and anaerobic digester gas are found in very small quantities. The two processes are incompatible, and putting them together would need a still lower temperature (<225°C) SMR catalyst.

- The goal of this project is to develop technology for directly converting biogas ($CO_2 + CH_4$) to a range of hydrocarbon products. The intent is to use an intensified process operating at mild conditions for a reduction in MFSP relative to the SOT. Traditional processes are high CapEx and not appropriate for small scales, where biogas is usually generated.

  Management: The project management structure is clearly outlined. USF and NREL, respectively, lead efforts in (1) synthesis and reactions and (2) characterization and design. NREL is also providing LCA/TEA support. These roles are appropriate considering the expertise of the various partners. The team has outlined a reasonable risk identification and mitigation plan. I was impressed that they are interfacing with such a large group of potential stakeholders, which is important for successful technology transfer. Overall, there are no concerns with respect to project management.

  Approach: The conventional process for biogas upgrading would use a multi-reactor train that includes a reformer, a shift reactor, separations, purification/cleanup, and a Fischer-Tropsch or methanol synthesis reactor. Classically, this is a capital-intensive process, and the integration between unit operations is difficult. The team proposes an intensified process with integrated—e.g., water-gas shift (WGS) and FTS-type chemistry—which decreases CapEx for reactors and heat exchangers, increasing distributed-scale viability. The team proposes coupling autothermal reforming with FTS in an intensified process, which is an interesting coupling because reforming is endothermic and FTS is exothermic, suggesting a possible coupling of the two. The core concept is the use of composite, layered catalysts that will enable reforming and FTS under similar conditions. It is an interesting concept whereby exothermic FTS in a zeolite-based outer shell could potentially drive endothermic reforming in an inner shell. Importantly, pore dimensions in the outer shell would generally permit methane and CO_2 to reach the interior reforming catalyst to produce syngas, which can then diffuse out to the FTS shell and form larger hydrocarbons. Once formed, these would be prevented from diffusing to the reforming core. The team is exploring various mixed- and stacked-bed configurations.

Impact: A distributed-scale technology for converting biogas into liquid hydrocarbons would be very high impact, so there is considerable potential here. One could imagine this as a way to reduce greenhouse gas emissions by converting methane and CO_2 into fungible liquid products while also creating a revenue stream for biogas producers beyond localized heat and power. The team is integrated with local stakeholders and potential technology adopters.

Progress and outcomes: This is a relatively early-stage project, but the team is already approaching their goals of higher hydrocarbon yields during biogas conversion. They have shown promising results in tuning bimetallic and promoter-doped catalysts for low-temperature methane reforming. They have also illustrated that they are able to prevent the reforming of large hydrocarbons (typically anticipated in a Fischer-Tropsch reactor) by varying the width of the zeolite shell. This is attributed to a longer diffusion path length, which is reasonable. The team is now designing new Fischer-Tropsch catalysts intended to operate outside of typical low-temperature, high-performance conditions and would be compatible with a reforming catalyst. Their characterization and activity testing work has provided fundamental insight into the nature of catalyst performance, and they have begun examining on-stream stability. They have initiated various types of bed combination strategies (mixed, stacked, multiple stacked, etc.), and results to date are informing TEA/LCA. Overall, this project has a fundamentally interesting core concept—designing layered catalysts to couple reforming and FTS in a single pellet. It is challenging, but high reward if successful.

- The key specific and measurable goal of the USF project is presented on slide 2 to develop the biogas-to-liquid (BGTL) process reducing CapEx and MFSP by 15% relative to the SOT and on the quad chart (slide 3) to develop a multifunctional catalyst to produce fuels and chemicals from biogas within an intensified process. The catalyst goal does not have any quantifiable targets. The goals seem aggressive—developing a catalyst and an intensified process simultaneously with a single partner. The ChemCatBio/NREL team is leveraged to complete the catalyst characterization and TEA/LCA tasks, which makes the project more achievable. This is a good management approach. The critical path tasks and roles are clearly defined. Key milestones include 100 hours TOS using real feeds and a 25% reduction in MFSP versus the SOT. The challenge of upgrading biogas of 1:1 CH_4:CO_2 makes the path to chemicals more attractive. The team identified several key risks: carbon yield, economics, oligomerization control, operational reliability, and real feed impurities. The mitigation actions involved were not as clearly explained. This milestone is more aggressive than one of the project goals. The team appears to have weekly meetings, quarterly DOE meetings, and regular industry input focused on the go/no-go criteria and project goals. The original plan of working with Big Ox Energy did not work out. Local and regional partners have been selected. The SOA process approach involved an SMR unit to produce hydrogen-rich syngas followed by a Fischer-Tropsch unit. This approach involves combining SMR and Fischer-Tropsch into one catalyst, which will make the process more intense and more efficient, advancing a clear DOE agency-level goal. The approach is to accomplish these traditional unit operations at the particle scale using concentric shell volume chemistry, where smaller syngas molecules reform in the inner core and oligomerize on the way back out of the particle. This approach actually fits into the engineered structure approach often used by commercial catalyst manufacturers to create extrudates and pellets, thus advancing the SOA for catalyst design as well. It would be nice to have a journal reference mentioned here supporting the concept and bolstering the idea. There should also be a strong approach rooted in intraparticle diffusion and heat and mass transfer analysis to clearly show the competing timescales for locating the optimal operating conditions. The stacked-bed and mixed-bed configurations are an excellent mitigation strategy just in case the multifunctional catalyst approach does not reach the targets. The BGTL process clearly advances and supports the BETO and technology area mission of developing and demonstrating transformative and revolutionary bioenergy technologies for a sustainable nation, as well as the BETO goals to develop commercially viable bioenergy and bioproduct technologies. The project supports the EERE Strategic Plan goal of enabling a high-performing, results-driven culture through effective management. The BGTL project supports and advances the Conversion R&D SMART Goal by 2021, completing the R&D necessary to set the stage for a 2022 verification that produces both fuels and high-value chemicals to enable a biorefinery to achieve a positive return on investment. The project addresses several key barriers in Synthesis and Upgrading—Ct-H. Efficient Catalytic Upgrading of Sugars/Aromatics, Gaseous and Bio-Oil Intermediates to Fuels and Chemicals, and Integration and Intensification Challenges—Ct-J. Process Integration (2), identifying impacts of inhibitors and fouling agents on catalytic and processing systems. In support of the Synthesis of Intermediates and Upgrading initiatives, BGTL is supporting the upgrading of bio-oils and syngas within the Chemical Conversion to Intermediates and Products subprograms. Finally, BGTL supports BETO's push for novel technologies by pursuing research on innovative technologies that can broadly enable the conversion of feedstock to fuels and products. The use of intensified auto-thermal reforming technology has been around for at least two decades in microchannel applications. The use of the tri-reforming FTS catalyst formulation to BGTL makes it potentially more innovative. Even more, combining auto-thermal reforming and Fischer-Tropsch in a process-intensified engineered structure at the particle level is a leap in innovation, and controlling the intraparticle heat and mass transfer gradients would be a breakthrough. The team has a very good and impressive understanding of how important the success of this project will be for BETO and the bioenergy industry at large, not only by reaching MFSP and efficiency targets but also with respect to waste stream management and byproduct stream revenue opportunities. The team will continue to train and graduate the next workforce; build industry partnerships; and publish, present, and apply for patents. The BGTL process has great commercial potential, and the project team has already started developing industry relationships regionally with both companies and municipalities. The network within ChemCatBio should be further leveraged to assist in this way. The nature of the current engagement with external stakeholders was not clarified. The team developed a low-temperature C-H bond-activating material at 723 K that was stable with moderate coke formation for 100 hours TOS. This was a very reasonable outcome, resulting in a 40% reduction in catalyst costs and energy usage. Control of intraparticle diffusion rates was demonstrated in a methane versus toluene activation experiment. The impact of indium promotion on iron dispersion and subsequent CH_4 by-production was interesting, as was the subsurface lattice oxygen lability. The presence of surface methylene groups appears to be critical for optimizing the timescales required for multifunctionality. At low conversion, where heat and mass transfer gradients can be managed and, hopefully, intrinsic kinetics are apparent, the team was able to demonstrate high-temperature Fischer-Tropsch activity for 70 hours TOS, which proves the current SOA for the industry partners on the project operating the two-reactor traditional process. The team did not see yet any catalyst stability or deactivation with this C-H activation technique, which is a major accomplishment. The most promising result was the combination of all this work in a stacked-bed configuration at lab scale operating at 773 K generating C3 material at 65% conversion, proving the process intensity with this proven reaction engineering approach as the risk-mitigating action.

- This project targets one type of very interesting biomass—biogas—and it is developing catalysts and processes that can convert biogas to fuels and high-value products. The team has a concrete management plan, and the progress is appropriate and could help BETO achieve its mission. The pandemic may impact the research progress, and it would be beneficial if the team would estimate the impact and develop plans to overcome it. The development of the core-shell catalysts seems to be interesting and probably provides a way to integrate separation and reactions. It could be beneficial if the team could conduct some fundamental research on these catalysts, and it could be helpful if the team could interact with the enabling groups within ChemCatBio and the other projects working on zeolite-based catalysts.

PI RESPONSE TO REVIEWER COMMENTS

- Overall, we appreciate the time, effort, and input from the reviewers. We also thank them for the many positive comments. We have included brief responses below to places requiring responses from us.

  Yields: There were a few comments about yields. We note that yields are on a mass basis, and oxygen in CO_2 is often a large component of the feed that does not end up in desired products. There are quantifiable yields that are part of the metrics for the project. The yields presented in the presentation and metrics are single-pass. It is possible that recycling would be used when implemented. As noted, this project is somewhat early stage, but it possesses potential for this application.

  Time frame: The pandemic did cause some slowdown. It is hard to quantify. In addition, some slowness was caused by the slow start to the project, which included delays by the verification visit in Budget Period 1. Related, we plan to publish papers on this topic very soon. The first ones are now in peer review.

  Challenges: We continually address the challenges of the ideal conditions for each reaction to be different. Codeveloping the catalysts to work toward similar conditions is a key differentiating component of this project.

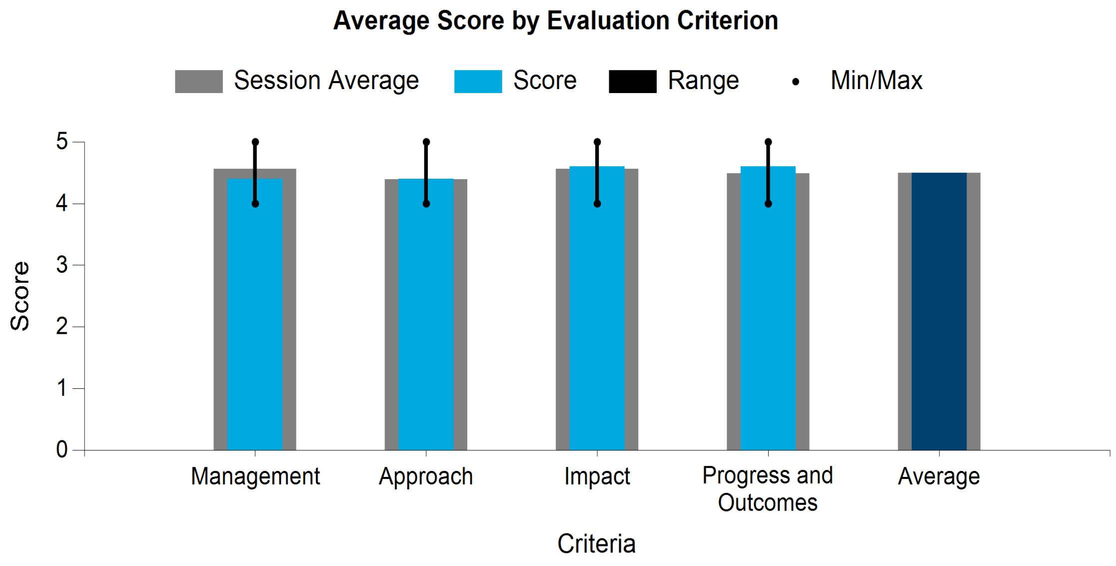
LOW-PRESSURE HYDROGENOLYSIS CATALYSTS FOR BIOPRODUCT UPGRADING WITH VISOLIS

Pacific Northwest National Laboratory and Visolis

PROJECT DESCRIPTION

WBS:	2.3.1.700
Presenter(s):	Karthi Ramasamy; Asanga Padmaperuma; Corinne Drennan
Project Start Date:	01/20/2018
Planned Project End Date:	09/30/2022
Total DOE Funding:	$785,000

In late 2017, ChemCatBio invited the industry to partner with national laboratories and leverage ChemCatBio capabilities. Visolis, a small company coupling bioengineering with chemical processing, answered the charge with a hybrid process to produce high-value monomers at near-theoretic yields. Visolis has previously demonstrated demonstration-scale (6,000-L) fermentation to produce an intermediate with low projected costs at a commercial scale. The development of hydrogenolysis to convert the bio-derived intermediate to the desired monomer was proposed to ChemCatBio. A major production cost in hydrogenolysis is the requirement for very high pressures—typical pressures for hydrogenolysis exceed 25 megapascals (MPa). In earlier work, Visolis and PNNL demonstrated complete conversion of the fermentation-derived intermediate with a selectivity exceeding 90% at 200°C and 12.5 MPa, but facilities capable of operating at such high pressures are expensive. Lower hydrogenolysis pressures improve CapEx and OpEx. The Phase I objectives were met by demonstrating a stable and robust hydrogenolysis catalyst in FY 2020 for the conversion of the fermentation-derived intermediate to high-value monomer at >80% selectivity under 5-MPa pressure. Objectives of the current Phase II effort are to understand and develop mitigation strategies for the feedstock impurities on the catalyst stability and to engineer the catalyst to extruded form for scale-up studies. The team will also provide TEA for a pilot-plant design using Aspen Plus process models and discounted cash flow analysis.



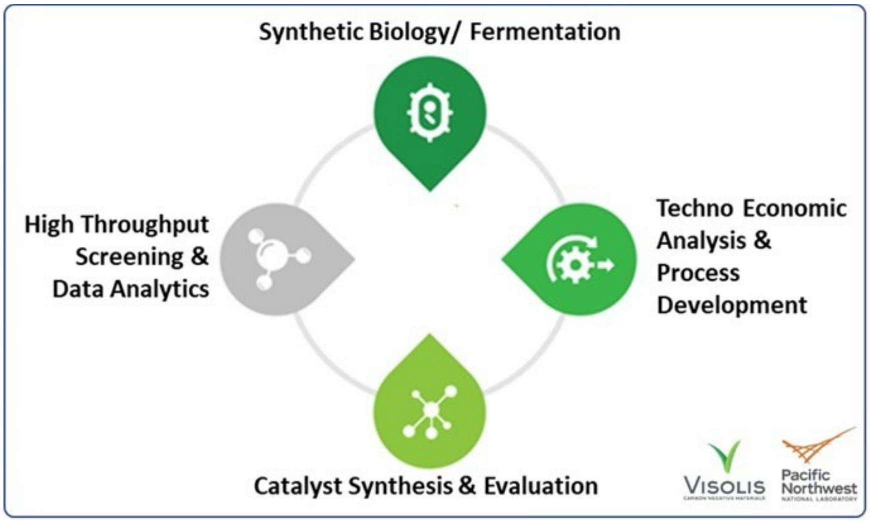


Photo courtesy of PNNL/Visolis

COMMENTS

- There is excellent management of the program, and we applaud the biweekly contact with the external startup company. This is a model program that can be used as guide for working with startup companies and other small- and medium-sized enterprises. This is clearly a well-communicated program based on results. Using the expertise of national labs for the catalyst development partnered with Visolis and their unique fermentation production product (C6 fermentation product) was a win-win situation. The combinatorial study was the right approach. The only question I had was were any nickel (Ni) commercial-type catalysts used, which can often be substituted for Pt, but, of course, may require higher pressures? Having a fermented C6 oxygenate for conversion has a lot of potential for impact—either for future C12, higher branched fuel additives perhaps, or unique feedstock for high-value chemicals like branched C6 acids, which are not available in today's market. Was selective reduction to aldehyde for use in aldol condensation considered for longer-chain material production? There is excellent progress on the catalyst, and the next steps are clear to reduce the catalyst loading, which is a key cost issue for Pt-based processes.

- The key goal of this Visolis project is presented on slide 2 and the quad chart (slide 16) and was written well in a specific and measurable way to develop a C6 sugar/sugar alcohol hydrogenolysis catalyst that can operate at pressures below 700 psi. The project has two key project managers who are coordinating work tasks from the PNNL and Visolis teams, respectively. The roles are clearly defined. The team has identified critical KPIs and targets as $P < 700$ psi, TOS > 100 hours, and $S > 85\%$. The risks and mitigation plans are not as clear, especially the criteria defined by Visolis as industrial-relevant. Key milestones include the cost-effective catalyst performing at all KPI targets with real impurities in the feed as extrudates. These are excellent, specific milestones. The communication appears to be frequent between PNNL and Visolis, with biweekly meetings and an annual face-to-face meeting. The approach of the Visolis/PNNL project is a great example of the accelerated catalyst and process development objectives of ChemCatBio. The goal is to accelerate lab-scale work to generate a pilot-scale process design package. This lab-scale acceleration is accomplished in Phase I by performing HTS, downselecting the most promising formulas and optimizing in a flow reactor while simultaneously checking TOS and stability, followed by pilot-scale, front-end design with model feedstock. The team should state if CCPC and ACSC are involved in preliminary catalyst recipe generation for HTS and whether the process is de-bottlenecked by including high-throughput synthesis activities as well. This is followed by Phase II work, which involves real feeds, extrudates, more TOS testing, and TEA modifications. This approach will definitely advance the art of hydrogenolysis catalyst formulations, most likely resulting in intellectual property creation as well as meeting ChemCatBio and BETO's objectives. The project supports and advances the BETO and technology area missions of developing and demonstrating transformative and revolutionary bioenergy technologies for a sustainable nation, as well as the BETO goals to develop commercially viable bioenergy and bioproduct technologies. The project advances the Biochemical Conversion Technology Area objectives pertaining to integrated conversion technologies by showing how new catalyst materials are moved into other BETO scaled-up system integration efforts. The Visolis/PNNL team does an excellent job of supporting the EERE Strategic Plan goal of enabling a high-performing, results-driven culture through effective management. The Visolis/PNNL project supports the Conversion R&D SMART Goal of by 2021, completing the R&D necessary to set the stage for a 2022 verification that produces both fuels and high-value chemicals to enable a biorefinery to achieve a positive return on investment. The project addresses several key barriers in Synthesis and Upgrading—Ct-H. Efficient Catalytic Upgrading of Sugars/Aromatics, Gaseous and Bio-Oil Intermediates to Fuels and Chemicals, and Integration and Intensification Challenges—Ct-J. Process Integration (2), identifying the impacts of inhibitors and fouling agents on catalytic and processing systems. The approach is innovative because it will deliver new catalyst formulations faster. More importantly, the approach is rooted in the traditional proper catalyst development steps, only carried out slightly quicker. The team did not express how big of an impact this work will have on the ChemCatBio objectives by showing compelling evidence for the acceleration development cycle proposal, which is exactly the type of validation work that was cited by the ACSC project as challenging. Most of the impact of the work appears to mainly benefit Visolis. Their core competence is rooted in synthetic biochemistry, so the partnership is a good fit. The project is directly tied to commercialization activities. The product has not been identified, so the full potential is unknown. It is assumed that there are not only negative CapEx implications with the higher pressures, but also some other penalty present that was not disclosed. The screening conditions were unknown, so the low-pressure objective may not have been the priority during this phase. It appears that the three development cycles—starting with monometallic, bimetallic, then support tuning—enabled a reasonable approach toward the selectivity milestone. The timescale of the work for combinatorial screening was not given, so it is hard to determine the catalyst design acceleration level. It was unclear how the excellent characterization work led to a new formulation cycle for HTS or for the flow reactor phase. The best results were presented on slide 12, which clearly and in a compelling way showed how the low-temperature Phase I catalyst performed much better at 4 MPa than the current SOA material at 13 MPa, which is the goal of the project, even for up to 350 hours TOS, which also reaches a key milestone. All of the Phase I objectives with model feeds have been achieved. It is important to understand what mitigation actions are in place when the extrudate version of the catalyst with real feeds are tested and the performance is compromised. The product streams were not disclosed.

- This DFA project supports the commercialization of lower hydrogenolysis for bioproduct upgrading. The major goal of the current effort is to understand and develop mitigation strategies for the feedstock impurities on the catalyst stability and to engineer the catalyst to extruded form for scale-up studies. Using a combinatorial strategy, the team developed the hydrogenolysis catalyst that meets their goal. It would be interesting to see how stable the catalysts can be in hundreds of hours. It would also be interesting to see how well the process can be scaled up. It could also be beneficial if the process can be modularized so that it can produce multiple high-value products to shelter the company from any possible big fluctuations of the market.

- This is a Phase II DFA collaboration between PNNL and Visolis; the goal is to develop a stable and selective hydrogenolysis catalyst that can operate at low pressures to convert a C6 intermediate to a high-value chemical monomer. The work is aimed directly at reducing the risk and cost for bioproduct process commercialization. This project is a great fit, allowing the commercial partner (with expertise in biosynthesis and metabolic engineering) to leverage catalysis expertise within ChemCatBio.

Management: The management structure and project position within the ChemCatBio space is well defined. The management hierarchy as well as the roles of individual players are clearly outlined. Each critical direction has an appropriate liaison in the relevant lab or industry partner.

Approach: The team is using high-throughput experimentation to quickly screen for appropriate materials, which are then deployed for optimization in a flow reactor. This seems a practical approach considering the pressure to identify a cost-effective catalytic upgrading strategy for a startup. The team is performing stability testing for >100 hours TOS, which is a good start for preliminary screening. Ultimately, studies may need to go beyond this time frame to de-risk scale-up, but it seems appropriate during initial screening for viable materials. Importantly, during Phase II, the team is placing stronger emphasis on impurity tolerance, evaluating engineered catalysts, demonstrating stability, and translating these insights into TEA and de-risking scale-up for pilot implementation. The team is encouraged to consider stability at lower conversion because high-conversion testing can give a false stability of on-stream performance.

Impact: At the outset of the project, the commercial partner identified a preliminary catalyst that is inherently active, but it requires 13 MPa of H_2 and is unstable, which makes it a nonviable catalyst according to TEA. The team has developed a new catalyst that works below the 5-MPa target and is more stable, directly impacting the MFSP for the Visolis product.

Progress and outcomes: The team used a combinatorial approach to identify a synergistic promoter in bimetallic formulations while confirming that monometallic catalysts offer inadequate activity and/or selectivity. Combinatorial screening also facilitated tuning the catalyst support to improve properties, and the team developed a stable catalyst that is 85% selective and operates below 5 MPa. The efficacy is attributed to alloy formation, which is supported by energy-dispersive X-ray spectroscopy mapping, where it is observed that particle composition matches alloy stoichiometry. This project has shown a reasonable reduction in cost moving from Phase I to Phase II. The Phase II work plan seems reasonable and is focused on further mitigating deactivation and reducing Pt group metal loading, with an emphasis on transitioning to engineered catalysts and demonstrating >500-hour stability.

- Although it is very good to team with small businesses, the presentation was a bit short on the kind of details a catalyst chemist wants to see. Nevertheless, the progress demonstrated for the catalyst life (350 hours) is impressive. Knocking 17% off the CapEx and OpEx is a big deal. Scaling up from powdered catalyst to an extrudate is an appropriate next step.

PI RESPONSE TO REVIEWER COMMENTS

- The project team appreciates the insightful comments provided by the reviewers. First, we apologize for not being able to provide detailed information related to the product streams, technical information on catalyst formulations, and risks and mitigation strategies during the peer review process. This is due to the constraints of confidentiality with the industry partner. Once the novelty is protected by patent, our goal is to make the information available to the public and document all the information in the data management hub operated by ChemCatBio. The statements by the reviewers on the project approach and the Phase I outcomes were very supportive and encouraging. The reviewers stated, “The approach is innovative because it will deliver new catalyst formulations faster,” “The approach of the Visolis/PNNL project is a great example of the accelerated catalyst and process development objectives of ChemCatBio,” and “The approach will definitely advance the art of hydrogenolysis catalyst formulations, most likely resulting in intellectual property creation as well as meeting BETO’s objectives.” High-throughput synthesis, screening, and characterization capabilities at ChemCatBio were utilized during Phase I of this project to identify the catalyst for low-pressure hydrogenolysis and demonstrated Pt-based catalyst as the successful candidate. The non-Pt-based catalyst, such as Ni, performed inferior even at the elevated operating pressures. Also, low-conversion experiments were conducted on the powdered catalyst in Phase I to understand the reaction mechanism of this hydrogenolysis chemistry. During Phase II, extended TOS experiments (>200 hours) at a low conversion level will be conducted on the engineered catalyst to demonstrate the catalyst stability performance. The goal of this project is to develop a low-pressure and water-tolerant hydrogenolysis catalyst to produce a specific high-value monomer from bio-derived intermediate, and we strongly believe the successful outcome of this catalyst development with fundamental understanding will facilitate the adoption of other biomass conversion technologies that are under the BETO portfolio. Also, this project supports ChemCatBio's objective to identify and overcome challenges in hydrogenolysis catalysis and make an impact in converting biomass and waste resources into renewable chemicals. In addition to this hydrogenolysis process, Visolis is developing a few other chemistries toward producing fuels and chemicals using the same C6 fermentation-derived feedstock as a platform molecule. This will provide the opportunity for Visolis to adapt to the market demand and price fluctuations.

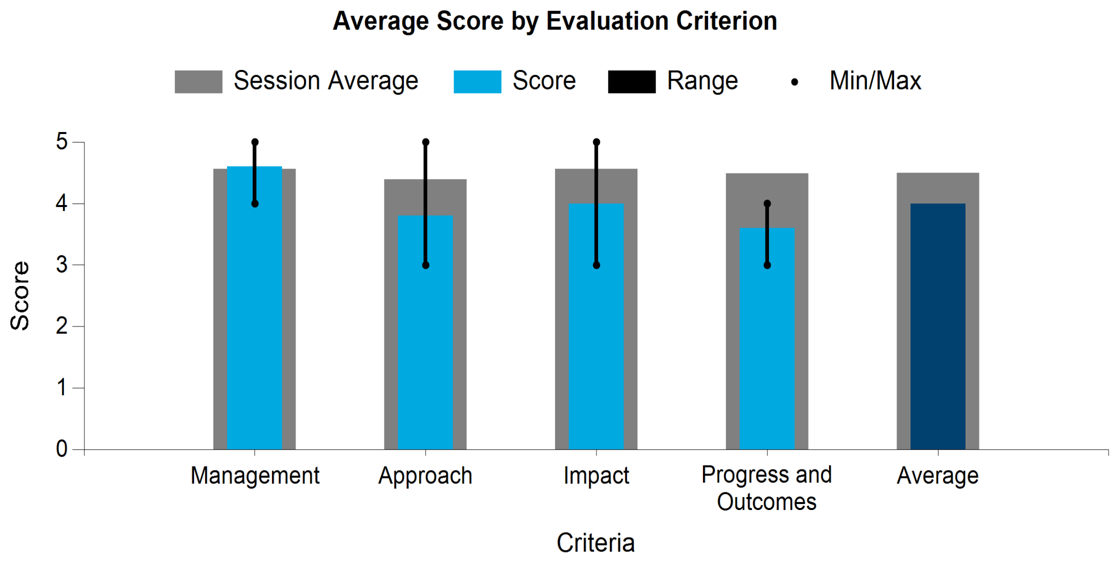
CATALYTIC PROCESS INTENSIFICATION OF BIO-RENEWABLE SURFACTANTS PLATFORM WITH SIRONIX

Los Alamos National Laboratory and Sironix

PROJECT DESCRIPTION

WBS:	2.3.1.704
Presenter(s):	Cameron Moore; Sheila Van Cuyk
Project Start Date:	09/11/2017
Planned Project End Date:	09/30/2022
Total DOE Funding:	$1,031,076

Surfactants are the key active ingredient in cleaning products, with long lists of additional builder ingredients added to boost function while maintaining product safety and shelf life. These builder chemicals increase product cost and volume and biodegrade poorly. Sironix Renewables has invented a new class of surfactants, called oleo-furan surfactants (OFS), which eliminate the need for these additional chemicals, reducing volume and resulting in a product that biodegrades readily. The OFS platform links the function of bio-based furan building blocks with natural oils to produce multifunctional and eco-friendly cleaning products. This technology gives improved performance, and by eliminating builder chemicals, it reduces the volume (and therefore packaging) by 30%. The end result is a reduction in overall energy consumption while producing a more environmentally friendly product. The Phase II joint research project with Sironix Renewables is designed to leverage the catalytic reaction engineering, catalyst development, and furan chemistry resources of ChemCatBio with the surfactants platform of Sironix Renewables to accelerate the DOE-invented and DOE Small Business Innovation Research-funded technology toward market commercialization. Technical goals include process improvements to achieve efficient scale-up of existing surfactants, the development of a new class of furan-based structures to address emerging market needs, and detailed TEA and LCA to measure market potential and environmental impacts.



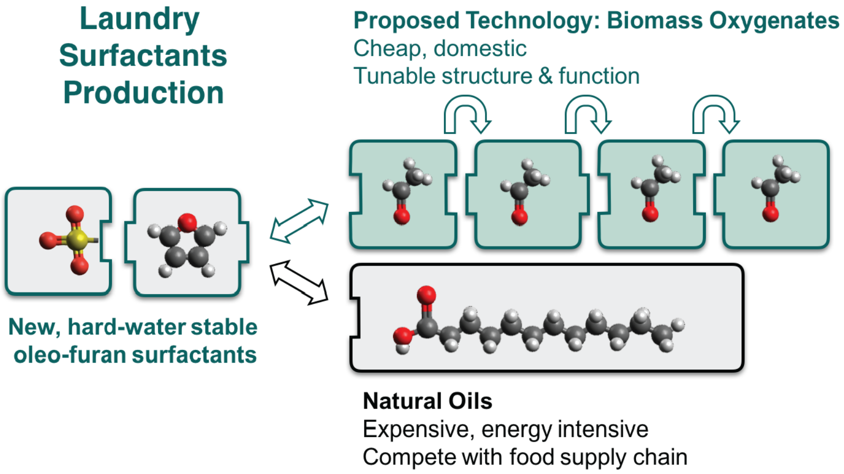


Photo courtesy of LANL/Sironix

COMMENTS

- This is solid at the management level for the project. The joint work between Sironix and LANL to progress catalyst development is a smart approach considering the catalytic expertise of this government lab. The initial approach using fatty acids was not desirable considering that fats and oils already have a mature end use for fatty alcohol-based surfactants, which are natural. The future work to address these questions by the team using low-cost biomass oxygenate addition to furan could make this surfactant competitive with the existing petroleum-based surfactants and is more in line with the objectives and goals of BETO. Replacement of linear alkylbenzene sulfonate (LAS) surfactants in the detergents market, in my opinion, is too big a challenge, but it would have high impact if successful. Numerous technologies have been developed in the past to try and replace LAS, such as methyl ester sulfonates, and even higher-performing biodegradable branched LAS. There is insufficient information to comment on the statement that this new surfactant can replace both existing surfactants and chelants in one formulation; however, chelants do more than sequester calcium to avoid precipitation of surfactant, as stated by the team. A suggestion to the team is to try and find some higher-cost niche markets for faster entry into the market at lower volumes once a sound technical result is achieved. Beauty care surfactants may be a better target for replacement. Isethionate surfactants, which are the dioxane-free alternative to alcohol ethoxylated sulfates, range in price from $3,000–$5,000/ton.

- The initial state of the project indicated that the process was getting a poor yield of unfavorable products. The 99% conversion with 98% selectivity for the reduction step is impressive. The project concern about the cost of natural oils may be misplaced. Many companies are investigating these for the production of renewable diesel, certainly a less valuable material (without incentives) than the surfactants that Sironix is pursuing. Thanks for answering this—we want a “tail” that is “tunable” in some ways to change the properties.

- The key goals of the Sironix/LANL project are presented on slide 4 and the quad chart (slide 16) to develop cost-effective furan-coupling processing strategies for the production of hydrophobic tails based on TEA relative to the fatty acid SOA pricing. The team could benefit from including other KPIs in the goal, outside of price, to help guide the R&D, such as durability and the size constraint for critical reactor units. The project managers are not specified directly. The key tasks and roles are identified between the two partners. Two critical risks were identified as incomplete conversion and poor product quality, with mitigation actions mainly to do more catalyst and process design iterations to find the optimal solution. It seems like this project management could use the design cycle acceleration approach to further align with the ChemCatBio objectives. The team provided an overall project timeline, with key milestones listed for Phase I: preliminary TEA, scale-up, and the final process design. The teams appear to interact monthly discussing risk issues. Because this is the case, there should be more than two project risk bullets provided. The approach is an iterative design cycle that closely mimics the ChemCatBio design approach (base chemistry, catalyst synthesis and characterization, flow reactor testing, surfactant production, and TEA), which results in unique, finished, comparable-performing surfactant formulations that will advance the SOA relative to fatty acid-based surfactants. The project will advance the BETO goals to develop commercially viable bioenergy and bioproduct technologies. The project has an opportunity to advance the Biochemical Conversion Technology Area objectives pertaining to integrated conversion technologies by showing how new catalyst materials are moved into other BETO scaled-up system integration efforts. The team does a reasonable job of supporting the EERE Strategic Plan goal of enabling a high-performing, results-driven culture through effective management. The project clearly advances and supports the Conversion R&D SMART Goal by 2021, completing the R&D necessary to set the stage for a 2022 verification that produces both fuels and high-value chemicals to enable a biorefinery to achieve a positive return on investment. It is still not clear how clean the raw feed streams need to be in order for this project to be economically successful. The Phase II timeline did not mention work with real raw feedstocks. The approach is innovative because it will result in new surfactant designs and corresponding processes with competitive economics. The team has been recognized as a bronze R&D 100 Award finalist and understands the impact that this technology will have on the biodetergent industry. The team's understanding of how their work will impact BETO is not as clear. This work fits right into Sironix's manufacturing strategy for commercialization, which is downselecting the best pathway from a TEA perspective, which could guarantee a long-term net present value benefit. The team made considerable progress in Phase I by improving the catalyst performance with very high yields to 2-dodecylfuran. Supports with moderately high acidity and metal loadings gave the highest yields in flow reactors with reasonable lower hourly space velocity for more than 50 hours TOS. These are important steps toward achieving the project goal of developing economic pathways. The zeolite framework was shown to break down during deactivation. The TEA part of the design cycle was not shared to understand the direction in the Phase II iteration and switch to ROHs. It is unclear if any of the milestones have been approached because the TEA information was not available and the project risk mitigation was not discussed.

- This DFA project supports the development of surfactants based on biomass called OFS. The project shows appropriate management and advancement. Bio-based products could enhance the sustainability of society. Commercialization exploration at the early stage is critical for the effort of realizing sustainability. Surfactants are widely used in many commercial industries and have many players. The quality of the final products and the reliable supply could play a key role. It would be beneficial if the team could use TEA to assess the economic output of their products. It could also be beneficial if the team could estimate a proper scale-up size for their products considering the market, the availability of the feedstock, and investment.

- This project is focused on enabling the production of furan-derived surfactants, supporting the development of a nascent startup (Sironix). These OFS eliminate the need for metal additives. The goal is to develop low-cost hydrophobic tails to compete with fatty acids and also to make new furan-tail coupling strategies, and the work is adequately informed by TEA. The specific challenges requiring new or improved catalysts are unclear.

  Management: This is a partnership between ChemCatBio/LANL and Sironix Renewables, and the roles of the project partners are clearly outlined. The national labs focus on conversion, synthesis, testing, TEA, and scale-up. Product quality testing is handled by Sironix. There are regular monthly meetings between the labs and Sironix, and handoffs between the partners are on a schedule. There is a clear risk identification and mitigation strategy. That said, it was curious for the team to highlight a risk with surfactant performance that appears to have already been resolved. Milestones are adequately tied to specific technical challenges, but it was unclear where the development of new catalysts for hydrophobic tails comes into the project timeline. The specific catalysis needs in this project are unclear—carbon-carbon bond-forming reactions, reduction, and tail synthesis are all mentioned, but I was not able to get a sense of the chemistries or catalysts required in each space.

Approach: This project has advanced from Phase I to Phase II since the 2019 Peer Review. The team is employing a build-test-learn development cycle, which seems to appropriately leverage domain expertise in various areas. The national labs are addressing catalyst synthesis, activity, stability, and scale-up/TEA, whereas Sironix is focusing on product performance. It was not clear whether fatty acid cost is a major challenge with this system, though it was cited as a main driver for needing to synthesize new hydrophobic tails. The data presented were a bit sparse, which is understandable for a startup; however, this makes it challenging to assess the science. I was concerned that the stability metrics may give a false impression of catalyst durability. The team is encouraged to examine catalyst performance at lower conversion levels. Similarly, it can be difficult to understand activity/selectivity compared at optimal conditions for one catalyst and (presumably) nonoptimal conditions for a second catalyst. There should be some way to standardize performance so that one can understand how changing the material impacts performance.

Impact: The technology provides a two-for-one solution: This is a renewable product that outperforms current surfactants, so it may have a competitive advantage and have decent potential for near-term commercialization. Research in this program has resulted in patent applications and a recognition by an R&D 100 Award submission. It is clear that the technology is receiving some attention.

Progress and outcomes: This project has resulted in the development of new surfactant precursors and selective HDO catalysts, and the team has considered sulfonation and property testing. Conventional copper chromite has been replaced with a new material from LANL that has improved selectivity under optimized reactor conditions, and the new catalysts have been deployed in flow reactors. It was somewhat hard to compare the performance of the catalysts where selectivity and activity appear to be compared under different conditions; further stability is benchmarked at very high conversion levels, where one usually gets a false impression of stability and sees a dramatic failure at extended TOS. The team may wish to consider the measurement of a low fractional conversion (maybe 10%) for extended periods on stream, where it is easier to see activity losses.

PI RESPONSE TO REVIEWER COMMENTS

- Response to Comment 1: We appreciate the reviewer's comments, and we appreciate the feedback on including other KPIs, such as durability and size constraints for critical reactor units, in our goals outside of price. This is an excellent suggestion, which we will consider further when performing TEA on newly developed routes to OFS products. We also agree that further risks could have been added, especially those that are associated with TEA efforts that are underway. A further risk, which we thank the reviewer for bringing up, is the effect of impurities present in feed streams that we have so far not addressed. This is certainly something we will examine as we narrow down potential feedstocks while working iteratively with our TEA. We recognize the difficulty in assessing the progress of Phase II given intellectual property constraints, and we will consider other ways to allow for more thorough technical review in the future.

  Response Comment 2: Replacing LAS surfactants is indeed a large challenge, and other markets, such as beauty care, are of interest to the project team. We recognize that more data could have been shared to support the claim that the OFS products can replace both existing surfactants and chelants in one formulation. The Sironix team has done extensive testing demonstrating superior product performance against many industry-standard surfactants, and we will consider how to better represent this work in the future. In particular, we will focus on performance areas relevant to personal care, such as skin mildness and foaming performance, in which OFS surfactants have also shown superior performance. By optimizing these performance traits, surfactants developed from this project will target the lower-volume, higher-value niche areas with a higher-performing, lower-cost surfactant compared with isethionates.

Response to Comment 3: We appreciate the recognition of progress within our project from the reviewer. We also understand the misunderstanding around the different catalysts being developed in this project because our aims have changed from Phase I to Phase II, and this could have been better presented. In Phase I, we specifically focused on the catalyst development for HDO chemistry of furan materials. For Phase II, our tasks are focused on developing catalysts for furan coupling chemistries. We regret that this portion of work was somewhat vague; however, we were unable to disclose the identity of the coupling partners and the associated catalysts at the time of the review due to ongoing patent submissions. In the future, we hope to disclose these details. Natural oil cost is only part of our concern with using these feedstocks; domestic availability is also a large concern, which we are considering when investigating other renewable feedstocks that can be used for producing hydrophobic tails for the OFS products. With respect to catalyst testing, we appreciate the reviewer's feedback concerning stability testing. Certainly, we can measure catalyst stability at fractional feedstock conversion levels, and we will consider this for future experiments and benchmarking.

Response to Comment 4: We thank the reviewer for noting how supply chain reliability is a key aspect to the success of this project. Estimates for the proper scale-up size of the products have been completed and were not included in this presentation. These estimates will be utilized for performing TEA, which is a deliverable toward the end of year one of Phase II of the project.

Response to Comment 5: We appreciate the reviewer's comment on the cost of natural oils. Ideally, natural oils available domestically would be used at feedstocks for OFS production; however, the oils most readily available in the United States, such as corn or soybean, do not inherently have the proper carbon chain-length distribution to function as surfactants for use in cleaning and personal care products. Other oils, such as palm and coconut, impart favorable properties to the final OFS product, but they are not readily available domestically and are associated with negative sustainability and environmental impact due to issues with deforestation and international transport. These are, in part, why the team is looking at tunable feedstocks from other sources.

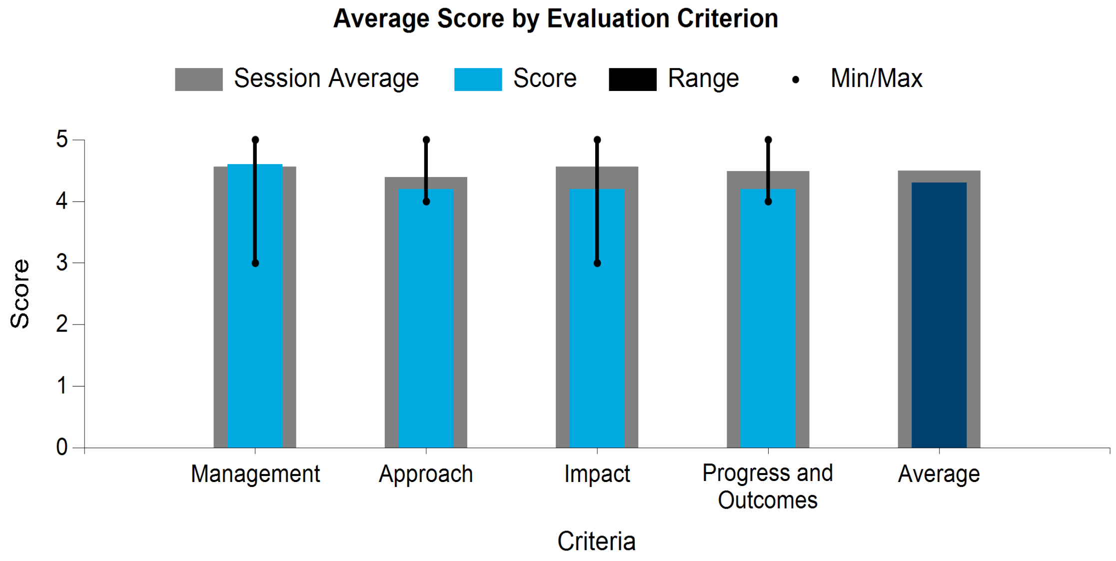
BIOMASS GASIFICATION FOR CHEMICALS PRODUCTION USING CHEMICAL-LOOPING TECHNIQUES

The Ohio State University

PROJECT DESCRIPTION

WBS:	2.4.1.404
Presenter(s):	Andrew Tong
Project Start Date:	10/01/2016
Planned Project End Date:	09/30/2021
Total DOE Funding:	$1,500,000

OSU is investigating the biomass-to-syngas (BTS) chemical-looping technology to produce syngas for chemical production applications from biomass under DOE Award #DE-EE0007530. The BTS process aligns with the programmatic area of interest of “Conversion, via biological, thermal, catalytic or chemical means, of acceptable feedstocks into advanced biofuels and/or bio-based products including intermediate and end-use products.” Compared to conventional biomass gasification processes, the BTS process eliminates the need for air separation units and tar reforming reactors, which leads to energy-efficiency improvement and CapEx reduction. The overall objective is to ascertain the potential of biomass gasification based on the chemical-looping technique through the mitigation of the possible techno-economic challenges in the steps of scale-up for commercialization. The scope of work consists of (1) designing, constructing, and operating a 10-kWth commercially scalable sub-pilot BTS system; and (2) completing a comprehensive TEA of the BTS process using methanol production as an example.



COMMENTS

- Chemical looping is a tantalizing technology that has been evaluated for the synthesis of maleic anhydride and a few other chemicals. The limitation to commercial applications has typically been the amount of material that must be circulated for each kilogram of oxygen that is provided. Using $FeTiO_x$ is interesting—does it remove any significant portion of the sulfur? Or anything else? Any buildup of K, Ca, Mg? Will the design be an FCC-type dual fluid bed scheme? The presentation mentioned countercurrent, but the figure shows cocurrent in the gasifier—wouldn’t countercurrent be better? Is there enough oxygen transported to make the process autothermal? What is the O-fed/biomass C ratio in the system? The management plan is a good way to get feedback from a variety of disciplines and stakeholders. The approach is appropriate—a stepwise study of each of the key features to build up to the complete system.

- The key goals of the OSU project are presented on slide 4 and the quad chart (slide 25) to develop an efficient thermochemical method for biomass conversion to syngas using a bench-scale cocurrent moving bed reducer catalytic gasifier. No efficiency targets were provided for approaching the project goal. Key milestones include some process KPIs, such as H_2:CO > 1.8, X > 95%, TOS > 100 hours, and updated TEA. The project is ending this year and was broken down into three major tasks: (1) unit design, (2) unit fabrication, and (3) unit operation. The key milestones were also clearly identified on slide 9. No project risks or mitigating action plans were provided. The project organization is extensive, including industry technical advisors, biomass suppliers, and potential commercial customers serving as advisors. The communication frequency between all of the partners was not disclosed. It is difficult to tell if the project approach will advance the SOA of bench-scale biomass gasification systems because it is based on the three basic process development principles of design, fabrication, and operation. The overall technical strategy of chemical looping the solid-oxide material is a clear advancement in the gasification SOA (i.e., tar reformer and air separation unit). The Nexant TEA suggests that the BTS process improves current gasification approaches. The details in the premise of those TEA assumptions is unknown. The BTS process supports BETO's push for novel technologies by pursuing research on innovative technologies that can broadly enable the conversion of feedstock to fuels and products. The technical approach of doing high-temperature WGS with gasification with a continuous catalyst regeneration system seems like it will be simple and innovative to scale up when finally applied. The OSU team realizes that this work could provide a low-cost, efficient pathway for BETO's biomass gasification interests. The opportunity to remove tar conversion and air separation units for traditional gasification units will have a major impact across the industry. The team has engaged industry stakeholders and has the potential to gain commercial interests provided the energy-efficiency, cost, and downstream unit design risks are adequately addressed, such as the syngas cleanup unit. The team was able to establish a unit-level process simulation model that showed reasonable experimental agreement with the 1.5-kW bench-scale unit. Cold-flow hydrodynamic flow tests in pipes were completed on the 10-kW lab-scale unit, which assisted in completing the reactor design. The team did an excellent job of including process hazards analysis and controls specs in the design. Some scanning electron microscopy characterization for bulk-phase redox catalytic properties were provided. It was unclear how this work altered the TEA next-generation design or operational approaches. The team showed results for the 10-kWth BTS reactor operating for 2 hours using corncobs. The preliminary TEAs for the BTS-to-methanol cases were completed with no final results provided. Milestones 7–9, which deal with fabrication and commissioning, were completed on time.

- This project aims to develop a chemical-looping process that produces syngas for chemical production applications from biomass. The team has an appropriate management plan for their research and advanced properly considering the impact of the pandemic. The accomplishment of a 10-kWth BTS reactor is impressive. The team is on its path toward the goal. The achievement of the goal could help the Catalytic Upgrading program complete its mission. The TEA could guide the research. It would be beneficial if the team could further consider how the whole looping can be well controlled and how the ability to control the process may impact the scale-up ability.

- This project uses iron oxide as an oxygen carrier in a chemical-looping gasifier to convert biomass into syngas. This decouples the oxidation and reduction of the catalyst, allowing one to operate without an air separation plant, which could significantly reduce CapEx and make biomass gasification viable at distributed scales. The overall goal is to develop a thermochemical method for biomass to syngas in a 10-kWth sub-pilot test facility on campus. There is a clear focus on demonstration and recyclability, and the team includes detailed TEA that considers the integration of the chemical-looping gasifier with a methanol synthesis process.

Management: The project structure is clear. The team is led by OSU, and there are two thrusts: demonstration in a sub-pilot facility (OSU) and TEA (Nexant). The management hierarchy and individual tasks within the aforementioned were less clear. For example, I could not determine whether certain partners were serving as researchers or in an advisory capacity. Milestones and go/no-go decisions are clearly defined.

Approach: The project focuses on the design, construction, and operation of a chemical-looping gasifier at the 10-kWth scale and TEA. Successful outcomes relate to carbon yield to syngas and thermal efficiency of the process. Technical challenges are associated with integrated system design, sub-pilot reactor costs, and downstream methanol plant integration with the BTS process. TEA is used appropriately to identify economically impactful areas of research. The team has identified that particle attrition and CO_2-rich syngas are the major issues with scale-up, and they are working to resolve these challenges. Technical details on the research were, at times, a bit light, and it was challenging to assess the approach in detail.

Impact: If successful, this project will allow cost-competitive gasification of biomass at the distributed scale, facilitated by a lower-CapEx facility. The team has performed 1.5-kWth bench-scale testing. As I understand it, the cost of air separation is a major challenge facing the production of fuels and/or chemicals through biomass gasification. A chemical-looping approach may conceivably mitigate that challenge. Because gasification is such a versatile approach for converting carbon-based feedstocks, the potential impact is high.

Progress and outcomes: The team has performed cold-flow model studies to validate reactor feeding; their hydrodynamic calculations have been validated. They have considered mechanisms for biomass feeding—an important challenge in solids processing. The team has designed a sub-pilot reactor and performed a safety review, suggesting it is close to deployment. The team has tested the redox stability of the iron oxide/TiO_2 particles, showing good durability. The team has performed initial demonstration work with methane and biomass feeds (corncobs) in the sub-pilot facility. They have also developed an attrition-resistant particle and initiated process-level analysis. Toward process intensification, they have successfully removed the tar reformer and steam reforming, suggesting an additional reduction in CapEx. Finally, they have demonstrated the production of syngas at >80% purity. Overall, the project seems to be making good progress toward the goals set forth in this project.

- This is well organized, and it is great to see the use of external gasification experts and end users for input as well as feedstock suppliers. The loop-type reactor system design is excellent for processes to maximize conversion. It is substantial for the direct generation of useful syngas in many applications in industry and for fuel groups. The team has made great progress at the sub-pilot scale. With all gasification processes I have seen in the past, there are challenges to scale-up, as is true with many programs in BETO. So far, it would seem that the project would be able to scale based on various data produced in the program.

PI RESPONSE TO REVIEWER COMMENTS

- Chemical looping for biomass gasification does require the circulation of particles through the system, similar to indirect heated gasification; however, unlike indirect heated gasification, where the solid media circulated serves only as a heat carrier, chemical-looping particles carry both heat and oxygen to the reactor with the biomass, which reduces the circulation rate in chemical looping. Uniquely, for the OSU moving bed approach, we reduce the particles from an Fe_2O_3 oxidation state when entering the reducer (i.e., the reactor where biomass is converted to syngas and the oxygen carrier is reduced) down to Fe/FeO, which means we consume nearly half the available oxygen on the oxygen carrier. This further reduces the circulation rate required for our system compared to other chemical-looping developments. The oxygen carrier flow to the biomass feed rate weight ratio (dry basis) is approximately 10:1. Compared to indirect heat gasification, which has a heat carrier circulation rate to biomass feed rate ratio of 27:1, the biomass chemical-looping system has a solid circulation rate nearly three times lower than the reference gasification method. In addition, because we can reduce the oxygen carrier to the Fe/FeO oxidation state, this allows us to achieve a high syngas purity, which I will discuss more in the follow point on cocurrent versus countercurrent moving bed flow.

- The primary objective in the oxygen carrier development is to develop a formulation that is resistant to deactivation through irreversible/non-regenerable reactions with the oxygen carrier. We have developed a formulation that is resistant to sulfur and alkali accumulation to allow it to sustain >15,000 oxidation and reduction reaction cycles; therefore, the sulfur will not be removed from the system using our oxygen carrier, but it will exit the reactor primarily as H_2S in the syngas stream. Alkalis have been shown to coat the surface for the oxygen carrier under severe conditions (i.e., when alkali content is equivalent to >1,000 times the biomass-to-oxygen carrier feed ratio); however, in this case, the oxygen carrier was regenerated to its original condition when oxidized with air.
- We have not seen any alkali build in our experiments; however, we have conducted specific tests on alkalis with specific focus on K and Na. Under high concentrations of Na and K (1,000 times greater than normal flow conditions), we observed a layer of Na and K on the surface of the particle when under the reducing condition of the reducer reactor. When subjected to air in the oxidation step of the combustor, the layer was removed, as shown in the scanning electron microscopy images; therefore, the alkalis in biomass are not expected to build up on the oxygen carrier because the oxidation step with air will remove any accumulation that may occur during the reduction step.
- The design will consist of a packed moving bed reducer for biomass conversion to syngas and a turbulent fluidized bed combustor for oxygen carrier oxidation with air. The operation is similar to FCC, with the primary difference being an extended standpipe and a second gas outlet that corresponds to the reducer reactor.
- A cocurrent flow pattern is better for the application of producing syngas. Countercurrent flow is better for applications of full fuel conversion to CO_2/H_2O (e.g., chemical-looping combustion) and/or for the production of pure gas products like hydrogen via a secondary oxidation step with steam. The general rule in a moving bed chemical-looping system is that you want your gas outlet to be located in a position where the oxidation state of the particles is complementary to the product gas you would like to make. For syngas as the product, the $Fe/FeTiO_3$ phase of the oxygen carrier has the higher CO/CO_2 and H_2/H_2O partial pressure compared to the other oxidation states of iron at equilibrium conditions. If a countercurrent moving bed design is used, the gas outlet will be located where the oxidation state of the oxygen carriers will be predominantly $Fe2O_3$, which will reduce the purity of syngas produced because Fe_2O_3 is thermodynamically favorable to convert syngas to >99% CO_2/H_2O; therefore, in designing a thermodynamically limited reducer reactor to process biomass to syngas, it is better to locate the gas outlet and the bottom of the moving bed to allow the gas to move cocurrently with the solid flow because, in this case, the phase of the oxygen carrier at the gas outlet will favor high-purity syngas production.
- Yes, absolutely. In a general sense, chemical looping, in this and most applications, represents the spatial separation of a gaseous oxidant (i.e., O_2 in air) from the fuel (i.e., biomass) where the oxygen carrier transports the oxygen and heat of the reaction. Because the oxygen carrier is undergoing cycle oxidation and reduction, in the overall net reaction of the combined reducer and combustor reactor, the oxygen carrier cancels out, and all you are left with is the oxidation of the fuel with oxygen; therefore, the net reaction is heat exporting, and autothermal operation is absolutely attainable with chemical-looping systems. The challenge is when we consider the need of a secondary oxidant that must be used, such as steam, to adjust the H_2/CO ratio in the syngas produced in the reducer and the maximum temperature limits we can subject the oxygen carrier to during its oxidation step with air. We primarily address this challenge through the consideration of how much support we load in our oxygen carrier (i.e., the heat

capacity of the solids). For our system, 40–70 wt % support in our oxygen carrier allows us to sustain the necessary operating temperature and heat supply to our reducer reactor to produce the syngas with a ratio >1.8 H_2/CO. Pressure is also a very interesting parameter we have assessed. Because gasification is a gas evolve reaction, it is thermodynamically less favorable at higher pressures. Adjusting the solid flow rate per biomass input is the similar approach to addressing the autothermal operating requirements. The optimum inert concentration remains in the range from 40%–70%.

- Efficiency target: I am sorry, we omitted this from our review slides this year. The target efficiency is to reduce biomass consumption by 13% compared to indirect heated gasification while removing the WGS and tar reforming unit requirements. We are also targeting greater than 47% reduction in steam consumption.

  Project risks and mitigation: The project risks and mitigation were addressed in the previous quarter of the project. The remaining project tasks are the operation of the unit and finalizing the TEA for the biomass-to-methanol case study. All are proceeding as planned. The primary risk observed in the previous quarters was the scheduling issues due to the pandemic and mechanical issues related to the biomass feeder, heating elements, and normal wear on the reactor unit. Each were repaired and put back into service. Operations of the sub-pilot unit are ongoing, with no issues observed.

  Communication with team: Communication with Nexant and OSU is frequent. It was biweekly during the first year of the project and is monthly currently. This was due to the initial process development the first year and updating the process design and finalizing the economics in the last year. For the independent review committee members, the meetings were once per quarter for formal meetings during the first 2 years of the project, when the sub-pilot unit was completing its design. The independent review committee meetings were reduced during the construction phase and due to the pandemic.

- One of the project objectives is to mature the chemical-looping technology for large-scale pilot testing through proving the reliability of the moving bed design for continuous operation (i.e., 100-hour test) and the sustained performance of the oxygen carrier and proving we can achieve the >1.8 H_2:CO ratio from biomass. This is a necessary step to gain industry support in the scale-up to a large pilot demonstration, which we have successfully done from the testing completed to date. From the sub-pilot testing completed, we have formed an industry team to support the next scale of the technology development.

- The TEA design basis was reported in Q2 of the project (March 2017). The biomass-to-syngas chemical-looping process will be designed to process 2,200 dry tons/day of biomass for crude methanol synthesis compared to indirect heated gasification subjected to the same biomass processing capacity. Three reference reports (DOE/National Energy Technology Laboratory (NETL) 341/020514, NREL/TP-5100-62402, and DOE/NETL 2011/1455) were used to analyze the reference indirect heated gasification base case and to provide performance and cost information for the upstream and downstream components of the chemical-looping biomass gasification process. The cost of the chemical-looping reactors was determined based on the reactor sizing (residence time estimations from bench-unit studies), and the reactor costing methodology was performed based on previously developed correlations for moving bed chemical-looping reactors (https://doi.org/10.2172/1149155). Further details on the specific equipment costing and sizing will be provided in the final TEA report; however, in general, the CapEx savings observed from the OSU chemical-looping system compared to the indirect heat gasification is due to the lower solid circulation rate (nearly one-third lower solid flow rate for the chemical-looping system compared to indirect heated gasification), removal of the WGS and tar reforming, and lower steam generation demand. The OpEx savings is due to the greater syngas yield and lower steam consumption from the OSU chemical-looping system.

- The main alteration is the reactor sizing and syngas composition obtained from the sub-pilot testing because these will influence the downstream syngas conditioning requirements and CapEx of the chemical-looping reactor. In addition, oxygen carrier attrition rate verification is an important factor that will be further verified in the 100-hour test because the makeup rate corresponds to an OpEx of the chemical-looping system. Previous and continued studies indicate that the attrition rate is well below 0.02% per cycle for the oxygen carrier we use in our system.

- This is an excellent point, and one which OSU has been heavily engaged in for the last 2 years—how to control the chemical-looping system for optimum performance under varying load conditions. Since 2019, OSU established a CRADA with DOE and NETL's Institute for the Design of Advanced Energy Systems (IDAES) to address this question for chemical-looping systems. Currently, we are working with IDAES to develop a dynamic model of our chemical-looping process based on the existing reactor models and particle kinetic models that we will then extend to dynamic control simulation. The work is currently directed to power generation applications with chemicals; however, it will establish the framework for the dynamic modeling of moving bed chemical-looping systems that can be easily extended to this biomass-to-syngas chemical-looping technology. We are in discussion with IDAES on extending our current studies to biomass gasification given the exciting results and test unit we have generated from this project.

- Outside of OSU and Nexant, the remaining team members are serving as advisory members. Technical input from Shell and ZeaChem was requested and provided when we designed the biomass feed system, but the overall objective of the involvement of these groups was to advise and support the next phase of the project demonstration.

- I did leave out the design methodology for the sub-pilot test unit to achieve the target 15-kW test capacity and the moving bed design principles used to determine the reactor size and the interconnecting standpipes for gas sealing and solid flow control. I hope that the supplemental slides provided may help with some the technical details that are missing in the presentation.

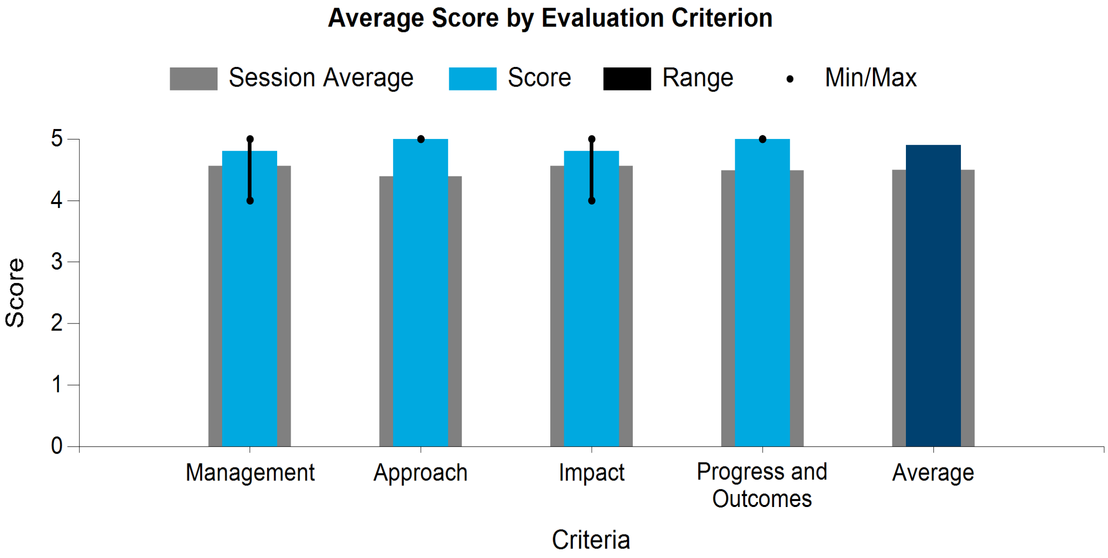
CONSORTIUM FOR COMPUTATIONAL PHYSICS AND CHEMISTRY

Oak Ridge National Laboratory, National Renewable Energy Laboratory, Pacific Northwest National Laboratory, Argonne National Laboratory, and National Energy Technology Laboratory

PROJECT DESCRIPTION

WBS:	2.5.1.301
Presenter(s):	Jim Parks; Tim Theiss; Zia Abdullah
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2022
Total DOE Funding:	$5,083,000

The CCPC is an enabling consortium of BETO that utilizes computational modeling to support the achievement of goals in ChemCatBio, the Feedstock-Conversion Interface Consortium (FCIC), the Bioprocessing Separations Consortium, and the Co-Optima initiative. The CCPC comprises six national labs (ORNL, ANL, INL, NETL, NREL, and PNNL), and the computational approach is multiscale modeling. This presentation will cover the management and approach of the CCPC and technical accomplishments specific to ChemCatBio (technical accomplishments for other consortia are covered in their corresponding sessions).



COMMENTS

- As always, the team has done a great job of managing a complex, critical area to input and guide PIs in the programs to accelerate progress toward the $3/GGE goal. I commend management for implementing the CCPC Direct Funded Assistance Program approach. The approach is clear. The massive amount of data and integration with the large number of teams has been accomplished seemingly with ease. This is a huge accomplishment. The feedback loop appears to be working well with the PIs based on responsiveness to data. The BETO-HPC: Dedicated High-Performance Computing (HPC) on Summit (the world's second-fastest computer) and Ridge will add a lot to the turnaround time on needed results. The impact of the program is clear and key to all the programs in BETO. The team has made outstanding progress. In industry, modeling is now the norm and adds high value to all programs in both commercial processing and consumer products. Although it has been a long journey from 2013 to now, and it continues to evolve and grow, the program's success in the future depends on this dedicated modeling effort. This is clearly seen in the various catalytic upgrading programs coupling a great computational program with outstanding catalyst teams.

- Management: The CCPC is integrated across various BETO programs and consortia. The management structure is clearly outlined, and it is appropriate given the far-reaching impacts of the CCPC. Nearly every project needs computational support. The management hierarchy is appropriate for managing such a large project. As I recall, the 2019 Peer Review suggested that industry partners may benefit from leveraging CCPC capabilities; the program has been responsive by launching new DFAs this year. The team has provided a nicely detailed risk mitigation strategy.

  Approach: The CCPC has to be nimble to provide support to new initiatives as they come into the BETO program, and the evolution of the program reflects this. The team uses multiscale modeling. This includes atomic-scale computational work to examine intrinsic structure and function, mesoscale modeling to capture transport phenomena, and full-scale reactor performance using multiphysics simulations. Insights at all of these scales are essential for understanding the performance of commercial reactors using pelletized or extruded catalysts. Different national labs lead individual tasks; this is appropriate considering the capabilities at each lab. There is a critical partnership between the CCPC, Catalyst Deactivation, and ACSC projects. This is necessary to develop and understand catalysts under working conditions, an important strategy for de-risking technologies. Process complexity is appropriately handled using a multiscale approach, with complexity captured at each scale as needed. Reduced-order and lumped models are also appropriate for developing tractable models. The HPC program provides access to world-class facilities and mitigates risks associated with access to computer resources. Considering the power of these facilities, access should open new opportunities for computational research that may have been formerly intractable—for example, large-scale data mining and machine learning.

  Impact: The team is using open-source software and is active in developing tools for this software. This is important because they can be accessed and used freely by anyone. The CCPC is also providing density functional theory data for the Data Hub/Chesapeake Bay, which is a very large impact for the catalysis community. The team has generated fundamental insights into how H_2 affects the Cu oxidation state, which is a critical activity descriptor for ethanol upgrading into higher olefins. This work highlights the interface with ACSC to compare theoretical models of the structure/oxidation state with, e.g., data from X-ray absorption near edge structure. The team is working on understanding Lewis acid and solvent effects on HMF production. The trends generally agree with experimental literature on effective solvents and Lewis acids. One wonders if this effort can predict a better solvent and catalyst than SOT for HMF production. The team's work with the deactivation program has helped to elucidate coke formation pathways during ethanol upgrading, leading to a strategy for minimizing the butadiene pathway. The mesoscale team is looking at catalyst (macro) structure impacts on performance. This is a collaboration with the Office of Science Basic Energy Science program and ACSC to help understand the role of porosity in predicting catalyst performance. I was interested in the updated effectiveness factor for cascading reactions, which is a nice update to conventional approaches. Reactor-scale modeling using multiphysics simulations identified risks associated with scaling the Pt/TiO_2 system due to thermal gradients, providing an important direction for future work in the CFP program.

  Progress and outcomes: The team has provided fundamental insights into catalyst stability, activity, and solvation. New access to HPC should expedite material discovery by enabling high-throughput density functional theory and machine-learning methods. This is already being applied for Mo_2C catalysts for bio-oil upgrading.

- The CCPC provides computational support to the other projects in the Catalytic Upgrading program. The consortium provides a clear management plan that enables the researchers from multiple national labs to conduct computational research on a wide variety of subjects relevant to the mission of the program. The research was conducted using proper computational approaches and has helped reveal the mechanisms governing catalytic performance, which can help design better catalysts. The impact of this project is mainly from two aspects: It helps see the detail of catalysis that the experiment cannot see, and this foundational research can help accelerate the design of catalysts. It could be beneficial for both CCPC and catalytic upgrading if CCPC can play a role more than an enabling activity. The advancement of computational methods and the construction of those HPCs (and quite a few of them by DOE) could open a new era for catalyst research. CCPC may produce a lot of data and tools during the research. It would be beneficial if these data and tools would be managed and distributed in a way to benefit the funding agencies and the public.

- The key goals of the CCPC project are presented on slide 2 and the quad chart (slide 39) to develop and apply computational tools that enable and accelerate the catalytic materials research and process development. The extent to which this acceleration and enabling effort is measured was not mentioned. The project goals mentioned on the quad chart appear to be more specific to the ChemCatBio catalysis and reaction engineering needs by providing multiscale kinetic information along with heat and mass transfer modeling. The CCPC may actually be the most collaborative consortium, touching almost every other consortium within the BETO portfolio and managed with a dedicated coordinator and technical liaisons with effective organizational structure. The key project milestone for ChemCatBio was to provide a multiscale model for the Pt/TiO_x CFP upgrading catalyst system. Deliverables to the milestone would include kinetic rates and regeneration cycles. The risks associated with the modeling complexity of real catalysts and not having the computer power to address this was mitigated by doing more experimental structure-function catalysis work, using lumped kinetics and working through the BETO-HPC. The communication frequency at which the CCPC interacts with the liaisons was not explicitly addressed.

  The consortium is highly collaborative, meeting with all of the IABs from the other BETO consortia. The team also has its own IAB and will be revamping that group in FY 2021. Several industry-led DFA programs involving the CCPC were launched in 2020 along with the HPC initiative. The consortium has published more than 40 journal articles and given more than 50 conference presentations since the last Peer Review, as well as public webinars. Further, open-source coding tools have been provided to the public. In terms of the SOA for the DOE BETO consortia—e.g., Bioprocessing Separations Consortium, Agile BioFoundry, FCIC, and CCPC—the CCPC continues to be a unique, powerful force across BETO by providing multiscale modeling tools and fundamental analysis/support from the atomistic to commercial scales. This approach of dealing with the issues of process design at all scales will continue to push the SOA. Further, the collaboration across DOE offices with BETO and the Advanced Manufacturing Office to collaborate on the HPC program is definitely an advancement in consortia SOA. The modeling of experimental data is how commercial process design occurs, so this consortium is critical to advancing BETO's goals and objectives.

  The CCPC supports the Conversion Technology Area objectives pertaining to integrated conversion technologies by showing how new catalyst materials are moved into other BETO scaled-up system integration efforts. The CCPC does an excellent job of supporting the EERE Strategic Plan goal of enabling a high-performing, results-driven culture through effective management. The CCPC has demonstrated support for BETO's Strategic Analysis Goals to ensure high-quality, consistent, reproducible, peer-reviewed analyses; to develop and maintain analytic tools, models, methods, and data sets to advance the understanding of bioenergy and its related impacts; and to convey the results of analytical activities to a wide audience, including DOE management, U.S. Congress, the White House, industry, other researchers, other agencies, and the general public. The CCPC supports the Conversion R&D SMART Goal by 2021, completing the R&D necessary to set the stage for a 2022 verification that produces both fuels and high-value chemicals to enable a biorefinery to achieve a positive return on investment. In support of the BETO Synthesis of Intermediates and Upgrading initiatives, the CCPC is aligned with the objectives of strengthening the Enabling Tools within the Computational Modeling & Analytical Tools as well as the Standards & Method Development efforts. The Ridge and Summit approaches with the HPC program to provide this extreme level of computing power is innovative in the configuration and hardware application. The multiscale modeling approach will always be innovative when coupled with experimental work to appropriately target the complexity. The CCPC has demonstrated how the impact of the consortium will impact the catalysis and reaction engineering community at all scales of modeling. At the atomic scale, the CCPC has provided fundamental insight into parametric experimental work that works across all scales. The atomic-scale work can predict the most optimized solvents and catalytic materials from fundamental descriptor correlations and computational screening. The multicomponent effectiveness factor vector concept is a good approach for the reaction engineering community and will be important for condensed phase analysis at the mesoscale. At the reactor scale, the team realizes their impact on predicting hot spots and other commercial-scale operational impacts on the CFP upgrading reactor. Other work outside of the ChemCatBio effort has shown commercial potential, especially with the recent DFA projects. This appears to be a good amount of direct industry engagement with the ChemCatBio-focused work. The reactor-scale work is ready for handoff to any established EPC ready to do FEL work on this process. The atomic-scale descriptor correlation work will set a standard criterion for downselecting solvents and eventually catalytic materials (e.g., volcano analysis).

In terms of ChemCatBio-focused work, the CCPC has made some progress toward enabling and accelerating. The atomic-scale analysis of Pt/TiO_2 materials must lead to the development of a fast-synthesis strategy, preferably a high-throughput method. Any mechanistic work dealing with surface water and its corresponding effects on reactivity is important. This was shown with the ketone condensation analysis. The computational screening work for HDO activity on transitional metal nitrides and carbides was fascinating and appears to be very promising. This is an example of an acceleration tool. The use of the graph neural network modeling technique on carbide surfaces for a model system, such as O_2 binding, is basic science and very useful, especially with such a common active site probe molecule. The extraction of the kinetic modeling parameters for Pt/TiO_2 is important work for TEA modeling as well as reactor design. There is also an opportunity to design experimental work to validate these parameters independently. The key end-of-project milestone of providing a multiscale model for the Pt/TiO_x CFP upgrading catalyst system has been reached with work at both the atomic scale (slide 33), mesoscale (slide 37), and reactor scale (slides 30–31). Further, the team received a “go” decision in FY 2020 for developing methods for extracting kinetics and using them in multiscale models. This was a major milestone.

- This project, dedicated to computational support for catalytic and other projects, is the kind of crosscutting project that seems to be the type of fundamental enabling work that is the core purpose of BETO/ EERE. As with some other projects, the management across different labs and applications is well structured, with a liaison designated for each program. The multiscale approach to catalyst modeling is very appropriate to such complex systems. Properly executed, modeling can help provide questions to be answered in experimental work and can provide answers to questions coming from experimental results. This synergy sets up a virtuous cycle of model/experiment that leads to greater understanding and, more importantly, better performance of the catalyst under study. The computational fluid dynamics (CFD) results seem particularly interesting; have they resulted in any changes to the reactor design or catalyst type? With the H_2 effect on Cu/BEA, can the same effect (Cu reduction) be seen with CO?

PI RESPONSE TO REVIEWER COMMENTS

- The CCPC thanks the reviewers for the feedback on our computational science R&D supporting BETO. We are pleased to see that the majority of the feedback comments were positive in nature, and we also appreciate the fact that specific positive feedback was provided for all scales (atomic, meso-, and reactor) of our multiscale modeling approach. Based on the supportive feedback, we intend to move forward with this successful approach. Regarding the comment on the extent of acceleration that our modeling effort is enabling for ChemCatBio, it has been difficult to quantify the acceleration benefit of our modeling program. We agree that understanding the extent would be valuable. We intend to seek more methods for obtaining quantitative and qualitative feedback on the value of our modeling for technology acceleration. Regarding the question of how frequently the technical liaisons interact with the CCPC, technical liaison interactions with other liaisons, task leads, and the CCPC PI generally occur on a monthly basis, and technical liaison interactions with the full CCPC team occur on a quarterly basis. Then, each technical liaison is interacting with the consortium supported at the frequency set by that consortium's meeting schedules. Note that interaction frequencies increase at critical times in the tasks and projects or if any issues arise that need to be addressed. There were some comments related to next-step readiness for technology transfer, including "The reactor-scale work is ready for handoff to any established EPC ready to do FEL work on this process." We intend to further engage with industry stakeholders to share our current model tool kit status and determine a path forward for the technology transfer of our capabilities to the bioenergy community.

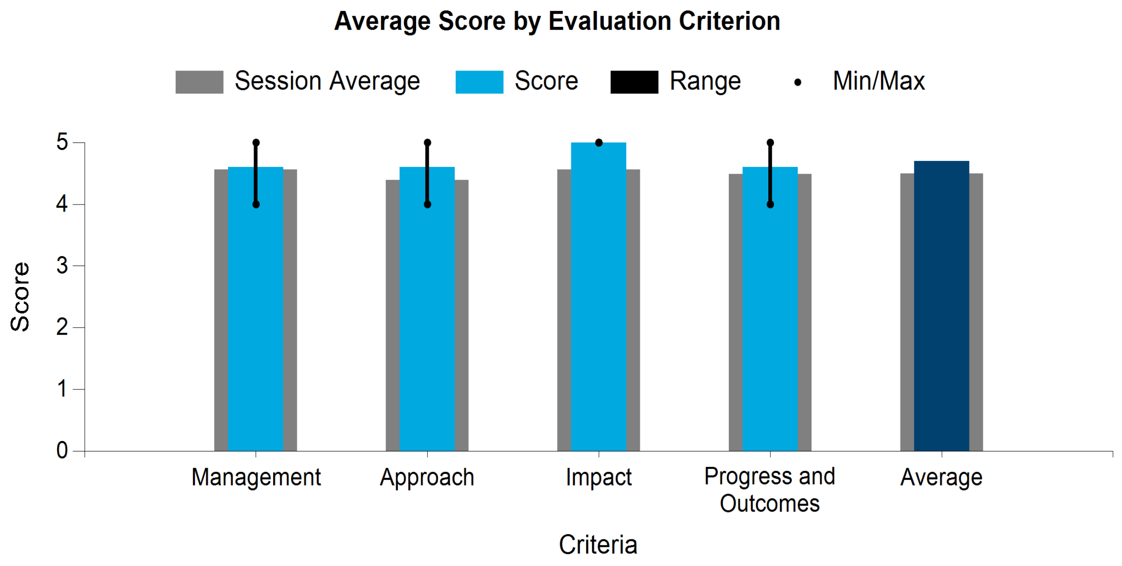
ANALYTICAL DEVELOPMENT AND STANDARDIZATION FOR BIOMASS-DERIVED THERMOCHEMICAL LIQUIDS

National Renewable Energy Laboratory

PROJECT DESCRIPTION

WBS:	2.5.2.301
Presenter(s):	Adam Bratis; Jack Ferrell; Zia Abdullah; Courtney Payne; Jessica Krupa
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2022
Total DOE Funding:	$1,875,000

This project began in FY 2014 to address the lack of standard chemical characterization analytical methods for bio-oils. Bio-oils are very complex and present numerous analytical challenges, yet reliable chemical information (quantification of both individual compounds and chemical functional groups) is needed to inform upgrading research and refinery coprocessing. In this project, analysis needs are first determined from engaging the bioenergy community. Next, standard methods are developed to meet these needs, and then they are subsequently validated via interlaboratory studies. Methods that are successfully validated (<10% variability) are then shared as laboratory analytical procedures (LAPs), which are free and publicly available. We have been tracking LAP use and have seen sustained usage, as evidenced by an average of 500 pageviews and 100 downloads per quarter, demonstrating the value of these methods to the bioenergy community. LAP methods that are particularly useful and reliable will be chosen for the next level of standardization through ASTM. We have recently achieved approval by ASTM for our carbonyl titration method. This method (ASTM E3146) is the first example of an ASTM standard solely focused on the chemical characterization of bio-oils. Work in this project is meeting the analysis needs of the bioenergy community and will ultimately help enable the commoditization of bio-oils.



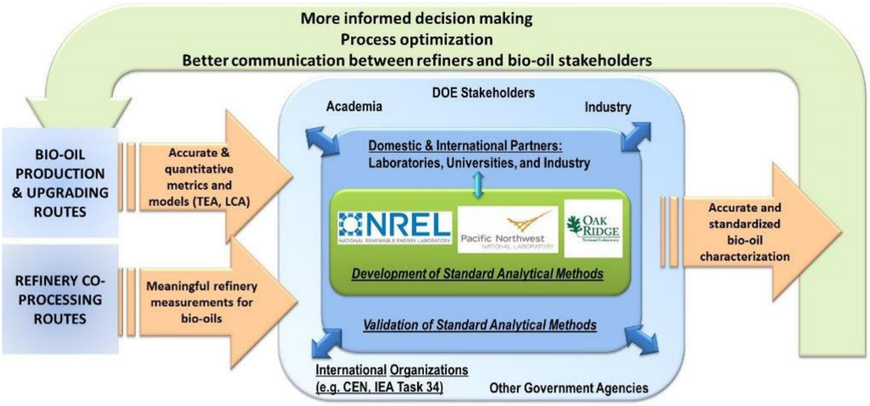


Photo courtesy of NREL

COMMENTS

- This is an excellently run and managed program during the years on a challenging task. Coordination among labs once again speaks to solid management. A solid analytical foundation is always key to future results, as defined here. The approaches are well defined and clear, and there are no issues. Why isn’t 2D gas chromatography-mass spectrometry (GC-MS) used when this is standard by petroleum companies and some consumer goods companies? Is this an outage in the DOE labs for routine analysis? Perhaps some additional investment in this area is needed. One other question is on the choice of ethylenediaminetetraacetic acid for chelant to study metal leaching. Many of the products of these processes are phenolic and catechol-type derivatives. These can be powerful chelants of metals, particularly if they have carboxylate or sulfonate functionality. Perhaps some analytical work on derivatized intermediates and products is justified for further understanding. We used sulfonation and TMSiCl or other derivatizing agents in the past for complex surfactant mixture analysis by gas chromatography. It is a nice way to shift the retention time of these reactive precursors for separating from aromatic, hydrocarbon, and olefin-containing species. It requires higher temperature-tolerant gas chromatography equipment and perhaps longer run times on gas chromatography. Standards exist, such as Tiron (trade name), which is a disulfonated catechol. There are also strong iron and other metal chelants in monomeric form or polymeric (work done by Lawrence Livermore National Laboratory in the past). Procter & Gamble patents on these chelants are US 8,921,299 and US 8,399,396 on these materials, as well as the earlier Motorola patent on the metal complex for the method of forming an electrically conductive polymer pump over an aluminum electrode (US 5674780). Without this work, the progress on bio-oils would have been slow. This is key to the impact overall, and the methods developed could have broader implications externally, as shown. There is excellent progress and a clear outcome to assist in driving programs on pyrolysis oils stabilization and processing via analytical tool and processing development.

- The characterization of complex product mixtures is central to understanding biomass upgrading, and bio-oil is a particular challenge that spans numerous projects. Integrating the many analytical techniques and developing protocols to carry out “standard” analyses appear to be successful in several cases. The aging test, in particular, is badly needed; is it applicable to a wide range of bio-oils—i.e., those containing widely varying O contents (even less than 5%, as in CFP oils)? The method has real-world application to commercial operations—designating how materials need to be stored and how accelerated tests should be done. The corrosion test also has real-world application, and it could be important in defining the correct materials to choose for reactors, transfer pipes, and vessels.

- The key goal of this analytical method development project is presented on slide 3 and the quad chart (slide 28) to develop standardized methods that support the commercialization of bio-derived and coprocessing liquids. Essentially, these will be additional methods that can be adopted by various stakeholders to develop quality specifications for the marketplace. The project could specify how many public standard methods are roughly envisioned to accomplish this goal as a way of measurement. The management of the project centers around compiling input from various stakeholders across government, national labs, academia, and industry, as well as international bodies of standards. There is no clear designation of a project manager for the team or single POC. The success factors were included on various slides. The risks to method development and the mitigation actions for those would be helpful as well. A key milestone is to submit a bio-oil analysis method to ASTM for voting by fall 2021. The communication plan involves frequent communication between labs and quarterly meetings with BETO, as well as active engagement at ASTM, which definitely takes commitment. The point person for ASTM engagement was not mentioned, and the manner in which industry is engaged directly is not as clear.

In terms of the SOA for method development, ASTM and the International Organization for Standardization continue to lead the pack, along with other private organizational standards, such as UOP and Merichem, placing them at the forefront as well. This project is already engaged in bringing new methods to ASTM, so this project is advancing the SOA. Further, the team is already coordinating lab round-robins and improving LAP published methods. The team should continue to organize the needs based on categorizing all of the key process sampling points in the two most critical paths for BETO 2022 verification, ensuring that the testing priorities are established. The team does an excellent job of surveying external and internal stakeholders. This project supports the BETO Strategic Analysis Goals to ensure high-quality, consistent, reproducible, peer-reviewed analyses; to develop and maintain analytical tools, models, methods, and data sets to advance the understanding of bioenergy and its related impacts; and to convey the results of analytical activities to a wide audience, including DOE management, U.S. Congress, the White House, industry, other researchers, other agencies, and the general public. The work also supports the Conversion R&D SMART Goal by 2021, completing the R&D necessary to set the stage for a 2022 verification that produces both fuels and high-value chemicals to enable a biorefinery to achieve a positive return on investment. The approach of compiling the analytical needs of a comprehensive list of stakeholders and developing a generalized solution or analytical method to meet everyone's needs, including ASTM, should always result in an innovative, useful published standard when complete. The project team has shown that they understand the great impact their work has on the bioenergy community by making LAPs publicly available and by standardizing methods (e.g., E3146) via ASTM, which impacts a broader audience. This also allows instrument vendors an opportunity to develop new technology offerings that include the standard methods as part of meeting the industry's needs. More importantly, the team understands that bio-oil cannot truly be commoditized until a quality specification is established that includes standardized methods available across the industry of third-party inspection and quality labs. The team has already gone through the cycle of engaging industry and pushing a method through the standardization system, which is often very difficult to do, so the commercial potential of the project has already been proven. The group has already published 10 LAPs, which is really good progress toward the goal of developing analytical methods for ChemCatBio that characterize key liquid streams. They developed an accelerated aging test method for the long-term storage stability of fast-pyrolysis bio-oils; a high-throughput, modified Folin–Ciocalteu method for measuring phenols; and the interlaboratory study completed for the current ASTM E3146 method. The group should provide more materials science insight into the corrosion test development demonstrating why certain ASTM methods with standard metal coupons are unacceptable from a post spent coupon and spent fluid characterization standpoint. It appears as though the group has reached the key end-of-project milestone early.

- The project aims to standardize chemical characterization and analytical methods for bio-oils. The development of standards plays a critical role in research as well as the economy and policymaking. The team has very effective management and has developed a series of methods and procedures to analyze the complicated bio-oil. It is very nice that the team is working on implementing their research outcome into ASTM standards. Such standards could have a big impact because they sort of set the rules for the whole community and especially clean up some uncertainties in analysis and characteristics. The accelerated aging tests are very effective to obtain the data needed in a much shorter time. Sustainable bioenergy is a world topic, and it would be beneficial if the team can reach out to the other important players in the fields and collaborate with them to set standards that can help advance the research on bioenergy—if it is okay with the funding agency's policy and regulations.

- This project aims to standardize bio-oil characterization, which is extremely important. Gas chromatography/GC-MS are widely used but are probably inadequate for detailed speciation; the field needs better analytical methods in this space. Overall, I was impressed with this project; I would love to see more of this type of work. It is immensely practical and critically needed, but it is not generally addressed in peer-reviewed literature.

  Management: NREL, PNNL, and ORNL are all doing the method development relevant to this project. The team is engaging with external partners to validate methods and then moving to share methods with all stakeholders working with bio-oil (research, industry, government, etc.). They are soliciting input from relevant stakeholders, which generally ensures impactful research. There is constant communication among NREL, PNNL, and ORNL, and the team has a long history of collaboration. It is good to see external stakeholders reaching out to solicit input and also provide input to guide the project. Overall, there are no concerns regarding the management.

  Approach: The approach is to provide analytical methods that give quantitative information about bio-oils as well as more robust speciation. There is a clear vision for what constitutes success in this project, and everything is systematic and rational. There is a good framework for analysis using a suite of analytical methods that can be appropriate to interrogating specific important aspects of bio-oil properties. Overall, this a great approach to solving a challenging analytical problem.

  Impact: This field is overly reliant on GC-MS for speciation, which is unreliable for a lot of these molecules because they may not have benchmarked fragmentation patterns in, e.g., NIST libraries, and it can be hard to purchase an analytical standard. This is an important direction for the biomass upgrading field, and this group is providing the ability to improve both quantitative and qualitative precision in bio-oil analysis. One needs to look no further than the impact of incomplete carbon balance closure on the CFP program to realize how important more robust analytical tools are to the field.

  Progress and outcomes: In addition to the bio-oil characterization methods, the team has developed an accelerated aging test, which is another area that needs standardization within the field. The ability to identify and quantify trace oxygenates is important due to their relatively high value (if they can be recovered) and/or their disproportionate impact on stability and performance in, e.g., jet fuels. Importantly, the methods being developed are low cost and robust/easy to implement, which is important for large-scale adoption.

PI RESPONSE TO REVIEWER COMMENTS

- We thank the reviewers for their time and feedback. We really appreciate the positive feedback as we are proud of what this project has accomplished. During the past 8 years, we have developed 10 standard methods as LAPs, which are free and publicly available. These methods represent the first of their kind as standards for the analysis of bio-oils, and, as such, these LAPs are frequently used by the global bio-oil community. Additionally, we have developed the first ASTM standard test method (ASTM E3146) focused on the chemical characterization of pyrolysis bio-oils, and we plan to submit a second method to ASTM in the coming months. The ASTM process was especially fruitful, as we brought in many different stakeholders working with bio-oils to participate in our ASTM task group for ASTM E3146. Through this work, we have built a reputation as leaders in this space, and we frequently interact with the bio-oil community, including researchers, industry, government agencies, standardization agencies (e.g., ASTM), international organizations (e.g., European Committee for Standardization and the International

Energy Agency), analytical service laboratories, and instrument manufacturers. Although we have built a cohesive team and we communicate frequently, the overall POC for the project is Jack Ferrell, and Earl Christensen is the lead for the ASTM engagement. Christensen is also the vice chair of the ASTM Committee E48 on Bioenergy and Industrial Chemicals from Biomass.

One of the questions was on providing more materials science insight in the corrosion test development—we collaborate with the Materials Degradation in Biomass-Derived Oils project (WBS: 2.4.2.301, PI: Jim Keiser), which is more focused on the mechanistic aspects of corrosion. Our project is focused on the methods development and on developing a screening test where the corrosion mass loss is correlated to the actual corrosion data obtained from project 2.4.2.301. Method development of the corrosion screening test is ongoing, with plans of publishing an LAP this fiscal year. On the question of chelants for metal leaching, ethylenediaminetetraacetic acid was chosen as a baseline to preliminarily confirm if the presence of a strong chelator will impact the corrosion of metals. We appreciate the suggestions for other chelators, and we plan to test some of the suggested chelators in future work. As for 2D GC-MS, we commonly run 2D gas chromatography in our labs, and we have considered the development of a standard method for 2D gas chromatography in the past. At that time, 2D gas chromatography was not as commonplace as it is today, and we did not think a standard 2D gas chromatography method would be widely applicable to the bio-oil community. Given the increasing availability and use of these instruments, we will revisit developing a standardized 2D gas chromatography method for biogenic liquids and their upgraded products. We agree that sustainable bioenergy is a worldwide topic, and we maintain international connections in this space. We collaborate with international entities on interlaboratory studies for method validation, and we had several international members in our ASTM task group. We also maintain contact with European Committee for Standardization to ensure that our method standardization activities are complementary on a global scale. Finally, the new aging test is only applicable to fast-pyrolysis bio-oils. Although our carbonyl titration method is applicable to a wide range of bio-oils, aging behavior is vastly different between fast pyrolysis and CFP samples. We are interested in the development of a more universal aging test, but more work is needed to understand the aging behavior of CFP samples and other non-fast-pyrolysis, biomass-derived intermediates.

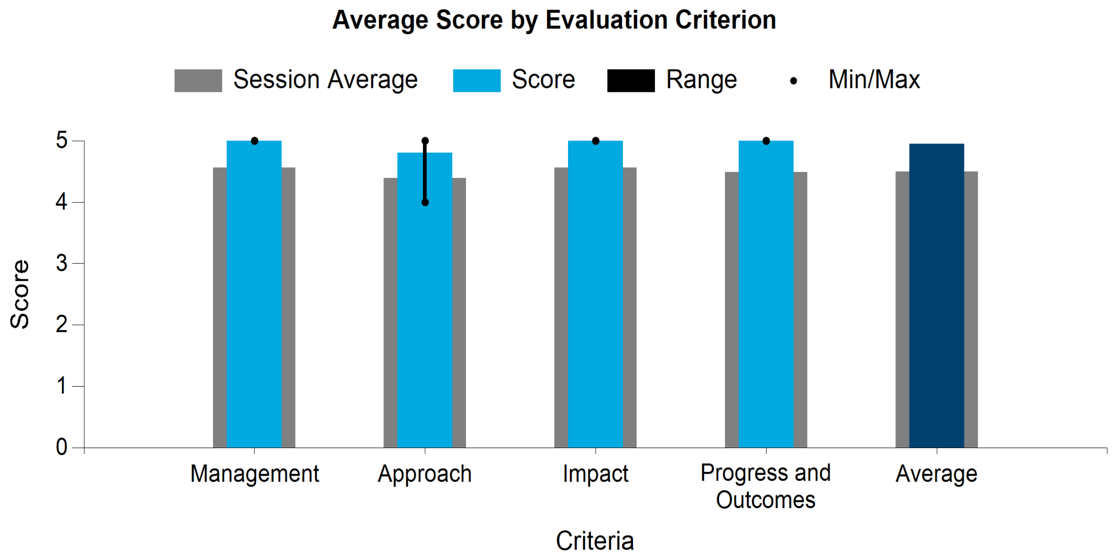
ADVANCED CATALYST SYNTHESIS AND CHARACTERIZATION

National Renewable Energy Laboratory, Argonne National Laboratory, and Oak Ridge National Laboratory

PROJECT DESCRIPTION

WBS:	2.5.4.304
Presenter(s):	Adam Bratis; Meltem Urgun-Demirtas; Susan Haas; Zia Abdullah
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2022
Total DOE Funding:	$4,500,000

The ACSC project—in close collaboration with ChemCatBio enabling projects, CatCost, and the Engineering of Catalyst Scale-Up project—(1) provides fundamental insight into working catalysts leading to actionable recommendations for all of the ChemCatBio catalysis projects, (2) addresses overarching catalysis challenges central to ChemCatBio, and (3) adapts and applies new synthesis methodologies and *in situ*/*in operando* characterization capabilities to meet the evolving needs of the catalysis projects. The outcome is a transition from empirical catalyst development to rational design through the prediction of materials with targeted properties based on advanced characterization combined with computational modeling and the synthesis of next-generation catalysts with predicted structures that yield demonstrated improvements in catalytic performance. In FY 2018, the ACSC helped to demonstrate the utility of the complete catalyst and process development cycle for DME to high-octane gasoline over metal-modified zeolite catalysts for the Upgrading of C1 Building Blocks project. In FY 2021, we will leverage the capabilities, expertise, and computational models established for this effort to target next-generation catalysts for ethanol to distillates for the Upgrading of C2 Intermediates project with enhanced performance in half the time.



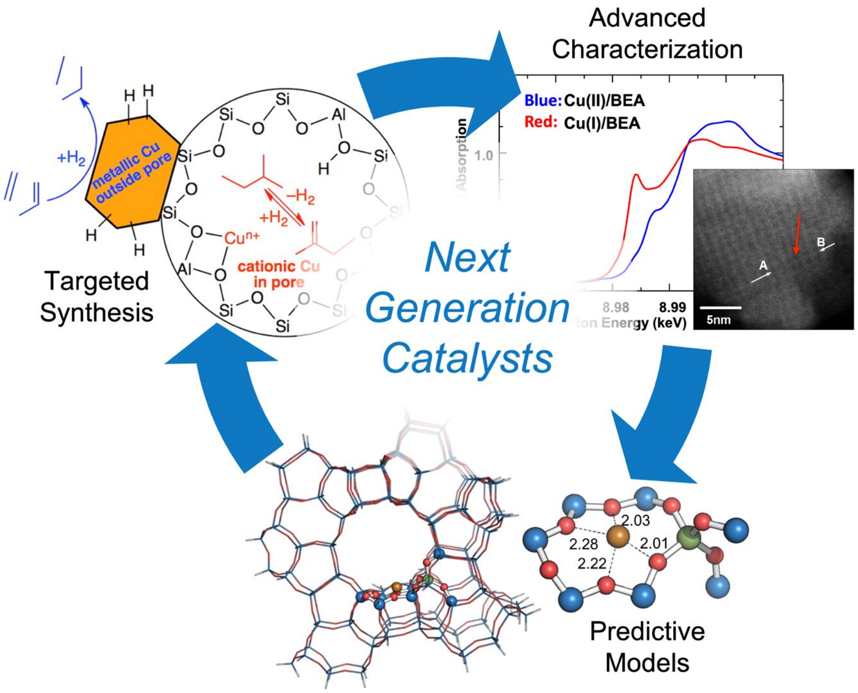


Photo courtesy of NREL/ANL/ORNL

COMMENTS

- The ACSC is an enabling consortium intending to provide fundamental insight leading to actionable recommendations to accelerate the catalyst design cycle. Their aim is to understand working catalysts. The ACSC provides controlled synthesis, advanced spectroscopy, and spatially resolved characterization (three core pillars).

  Management: The program is responsive to feedback from partner consortia, stakeholder projects, and the IAB. The active management structure is clearly outlined; leaders in synthesis, spectroscopy, and spatially resolved characterization are clearly identified, and appropriate liaisons are designated for mature collaborations. There are multiple modes of interaction with the ACSC, providing how projects can access ACSC infrastructure according to their specific needs.

  Approach: The approach focuses on identifying active sites under working conditions to help inform computational modeling for predicting better materials, developing new catalysts, and verifying their performance. The team is focusing on a current challenge of accelerating the development of catalysts in the C2 upgrading platform. A key capability in the ACSC is the ability to synthesize model catalysts with well-defined active sites, which is essential for good experimental characterization of structure and function for comparison with computational models. The team is tackling new challenges as they arise. For example, there is a new focus on electrocatalysis, and they are considering lower-cost metal phosphides and carbides for use in the CFP program.

  Impact: The 2019 Peer Review indicated that industry partners would benefit greatly from access to ACSC capabilities; this is occurring through DFA projects. The ACSC clearly impacts catalytic upgrading projects across ChemCatBio. Affiliated programs, such as Co-Optima, also benefit because the need for better synthesis and characterization is pretty ubiquitous. Some clear examples of ACSC impact are their contributions toward understanding the active state and function of Cu sites in catalysts used for C1 and C2 upgrading. A strategy for the regeneration of metal carbides under mild conditions would be a nice impact. This team is producing high-quality contributions to basic catalysis science.

Progress and outcomes: The team has demonstrated a complete catalyst development cycle by developing next-generation catalysts for C1 upgrading in the DME-to-high-octane-gasoline pathway. This required collaborations across various projects and consortia, ultimately leading to direct improvement in fuel properties through catalyst design. ACSC work is focusing now on identifying active sites in Cu/Zn/Y catalysts, and characterization has revealed atomically dispersed cations under reaction conditions, which is important to understanding their function. Overall, this is a good example of providing excellent synthesis/characterization to build understanding of how materials are working under reaction conditions. The ACSC team was instrumental in understanding how potassium impacts the deactivation of Pt/TiO_2 catalysts; the project is doing a good job of connecting model and real systems, and the potassium study is one good example of such. Efforts to understand how water impacts the structure and stability of catalysts is a positive direction given the ubiquity of water in biomass processing. The team designed and deployed a scalable flow synthesis method, which should help to provide quantities of materials required for commercial processes.

- Characterization is critical to advancing the understanding of catalyst function, kinetics, and structure. This program appears to be having impact across numerous projects and technologies, fulfilling its overarching goal. With samples moving back and forth, “chain of custody” and sample identification is quite a complex and challenging management function. Designating an individual as a single-point liaison for each is a good way to address this challenge. The question that I was frequently asked when I proposed using an “exotic” analytical technique was: “What will you do if you get the answer?” For at least the Cu/BEA system, it appears that the characterization helped influence the progress, where Ga and Zn were identified as candidates for improving dehydrogenation. The *in operando* evaluation of Pt regeneration confirms what Gabor Somorjai proposed many years ago—I wish I had access to more *in operando* techniques in my day.

- There is excellent management of the team. The results of solid management are clear from the progress of the catalyst programs. The excellent feedback loop via monthly meetings and joint decision-making with the teams makes for rapid progress and the ability to shift program(s) as needed to improve catalyst systems. Catalyst improvement is key to the overall BETO program in many different conversion areas. Industries—both chemical and fuels—rely heavily on catalyst technology, and this team’s work will have long-term impact in both biofuels and existing chemical and fuel processes. I did have a question for the team: Although none of the programs are using low-temperature olefin metathesis, was this considered by the catalyst team or other teams that they work with for conversion of olefin and functional olefins to higher analogs? This type of catalyst has clearly moved out of the pharma-only arena into chemicals in the last 10 years, and it seems to be a missed opportunity area for BETO and the government laboratories. Clear results are shown by the team in terms of catalyst selection and cycle time reduction across numerous programs within BETO. The impact on external companies and partnerships is clear. The pace of publications continues to inform the industry and clearly proves the team’s world-class catalysis synthesis and characterization. The team has attracted some big names in industry as both partners and external IAB members. No outages are seen, although some catalyst development of some of the bio-derived materials may not be the best use of the group due to the challenging economics, even with the best catalyst system they can develop; however, the team is doing great work even in those programs.

- The ACSC project provides advanced technologies and abilities to characterize and synthesize catalysts critical for the mission of the Catalytic Upgrading Technology Area. The advanced characteristics technologies help rationalize the design of catalysts with the other enabling groups, such as CCPC. The advanced synthesis capability enables the specific research projects to possess the catalysts that they want, a critical step in investigating catalytic performance in experiments. The ACSC has shown impressive progress when collaborating with the Upgrading of C1 Building Blocks project. It would be very interesting to see their progress in the Upgrading of C2 Intermediates project. It could be beneficial if the three enabling groups could play a more independent role in the catalytic upgrading program. It could also be beneficial if the ACSC could consider sustainability and affordability when developing catalyst synthesis. In addition, it would be beneficial if the ACSC would leverage their experience to develop some tools or standard operating procedures that can help the researchers with the high synthesis skills to prepare the catalysts.

- The key goal of the ACSC project is presented on slide 3 and the quad chart (slide 28) to provide fundamental insight that leads to critical R&D decisions to take action. This is a very clear, succinct goal, and the ACSC embodies the core of the catalysis scientific principles and fundamentals of ChemCatBio. The team did an outstanding job of providing quantitative targets to this goal with baseline process KPIs, targets, and fundamental catalysis metrics. For most of the ChemCatBio portfolio, the experimental work centers around deactivation principles, which really explains why CDM became a key enabling project of its own. It is understood that the ACSC has other distinguishing objectives from CDM. It is good to see tight, close-knit collaboration, even if it has the optics of having a little redundancy. The leaders across ChemCatBio should continue to promote the same unifying messages to focus and strengthen the consortium. The ACSC should continue to clarify how the project contributes to the accelerated catalyst and process development cycle. It was good to hear half the development cycle time stated. The management plan centers around offering three families of advanced catalysis tool platforms: rooted in spectroscopy, imaging, and synthesis. The lead PI appears to serve as the project manager or team POC, organizing meetings and driving task completion. The risks associated with instrument reliability and mitigating strategies were not discussed. This should be at the forefront of the project management metrics for such a service organization, along with the monitoring tools and strong preventative maintenance program.

  The key project milestones mentioned on the quad chart (slide 28) show how fundamental catalysis insight from the ACSC/CCPC collaboration drives the design and development of a generation of noble metal-free catalysts for the CFP pathway. This is clearly a cost-savings milestone. The ACSC should consult the TEA team on estimating the financial impact of this work on MFSP. The close collaborations fostered by the ACSC (e.g., CCPC, CCM, Advanced Photon Source, Systems Development and Integration) have led to significant reductions in the final MFSP estimations. There appears to be some interactions with the ChemCatBio IAB at some frequency. The level of engagement with the IAB and other industry partners within ChemCatBio is quite impressive, as presented on slide 13. There continues to be direct interactions with industry, with more than 50% of their collaborations funded via the directed funding opportunity (DFO) program. The communication plan involves monthly meetings and annual face-to-face interactions. The group has generated 14 papers and 5 patents within the last year. On the impact slide 15, the team has also provided a webinar and continues to communicate data into the Data Hub. In terms of SOA synthesis and characterization tools, which are generally housed in universities and national labs, the ACSC is clearly part of the SOA. Their approach is to be as flexible and responsive as possible to the ChemCatBio client. This will definitely help move BETO closer to its goals. The team's perspective on slide 9 that it is difficult to quantitatively evaluate how much ACSC contributes to the cycle development acceleration is greatly appreciated and honest. It was mentioned that the normal baseline can take about 3 years, with a goal to complete the actionable work within 1.5 years. This is the foundational premise of ChemCatBio and remains the reason behind the approach criteria. The team should continue to strive to find experimental ways to speed up characterization and synthesis. This is why the close cooperation with the CCPC is paramount to introduce the learning algorithms into the approach where experimental characterization can take more of a validation role in the future.

  The ACSC supports the BETO Conversion Technology Area objectives pertaining to integrated conversion technologies by showing how new catalyst materials are moved into other BETO scaled-up system integration efforts. The ACSC has demonstrated support for the BETO Strategic Analysis Goals to ensure high-quality, consistent, reproducible, peer-reviewed analyses; to develop and maintain analytical tools, models, methods, and data sets to advance the understanding of bioenergy and its related impacts; and to convey the results of analytical activities to a wide audience, including DOE management, U.S. Congress, the White House, industry, other researchers, other agencies, and the general public. The ACSC supports the Conversion R&D SMART Goal by 2021, completing the R&D necessary to set the stage for a 2022 verification that produces both fuels and high-value chemicals to enable a biorefinery to achieve a positive return on investment. In support of the BETO Synthesis of Intermediates and Upgrading initiatives, ACSC is aligned with the objectives of strengthening the Enabling Tools within the Computational Modeling & Analytical Tools as well as the Standards & Method Development efforts. At this stage, the use of these advanced techniques to generate a new generation of catalytic materials is inherently innovative, and the team has the intellectual property to prove it. The fact that the core premise of this group involves employing advanced characterization techniques to understand working catalysts makes the approach relevant and innovative. The ACSC understands its critical role in the U.S. R&D catalysis community in how they stress their capabilities with working catalysts versus modeled surfaces only. This is why the team's impact can be seen in the industry collaborations, providing answers to difficult fundamental catalysis questions. Further, the data will be shared online for the bioenergy community to take advantage of the knowledge. The ACSC has already proven that their impact has great commercial potential in their DFO collaborations with industry, which informs ChemCatBio.

In so many ways, the ACSC has made great progress toward its project goals to provide fundamental insight that leads to R&D action, especially with project funding arriving in late 2020. Some of the many notable achievements include:

- Active site identification, followed by suggesting co-metals for the design of bimetallic Cu-X/BEA DH catalysts resulting in the synthesis of next-generation C4 DH catalysts with improved activity and selectivity.
- Coke characterization leading to the optimal oxidative regeneration temperature for Cu/BEA spent catalysts from DME transformations.
- Identification of the Cu surface agglomeration mechanism during ethanol conversion over Cu-Zn-Y/BEA leading to a change in regeneration procedures.
- Active site identification of metal and acid sites for methanol coupling-supported Cu catalysts resulting in optimized synthesis protocols.
- Elucidation of the dispersive impact of oxidative regeneration cycles on Pt/TiO_x spent catalysts from *ex situ* CFP upgrading reactor beds resulting in changes in regeneration protocols.
- Determined surface basicity from water-exposed MgO (111) surface as an active site during aldol condensation, impacting the decisions on how to regenerate, verifying a low-temperature, continuous synthesis procedure for transitional metal carbides that resulted in increases in reverse WGS activity, regeneration of Mo_2C without overoxidation, and loss to sublimation.
- Characterization of hydrogen evolution reaction activity in CuP_x materials leading to applications for electrochemical CO_2 reduction.

The team has very impressive technology development stories that can be bolstered by first always sharing what the original approach/decision/direction was before the ACSC became involved to clearly quantify the value. The study of transition metal carbides has great potential for replacing noble metal-based CFP catalytic materials. The ACSC has devoted a great effort to further understanding these materials, although the milestone has not yet been reached. Another non-noble-metal-free platform should be proposed as an alternative approach and/or an alternative synthesis strategy for the carbides to mitigate any risks.

PI RESPONSE TO REVIEWER COMMENTS

- We thank the reviewers for their thoughtful insight and constructive feedback. We appreciate the positive comments regarding our quantitative catalyst development targets developed in collaboration with the ChemCatBio catalysis projects and our TEA team; the strong interaction we have had with our industry partners, particularly through the ChemCatBio DFO projects; and our overarching goal of contributing to the acceleration of the catalyst and process development cycle by providing fundamental insight leading to actionable recommendations. We agree with the reviewers that the ACSC project should continue to clarify how we contribute to the acceleration of the catalyst and process development cycle, and we are looking forward to quantifying this acceleration with the Upgrading of C2 Building Blocks project this year in comparison to our previous collaboration with the Upgrading of C1 Building Blocks project, which served as a baseline for the complete development cycle. We also agree that there are risks associated with instrument reliability, and the mitigation of these risks through a strong preventative maintenance program coupled with our development of complementary characterization techniques is an important goal of the program. We will continue to maintain and strengthen our collaborations with the TEA team (including the CatCost tool) and the CCPC to ensure that our efforts have a measurable impact that considers costs and to move toward predictive models that can further accelerate catalyst and process development. Finally, we will continue to evaluate metal carbide catalysts as replacements for noble-metal-based materials by focusing on developing a strategy for regeneration under mild conditions and identifying other non-noble-metal systems that could serve as an alternative to mitigate associated risks.

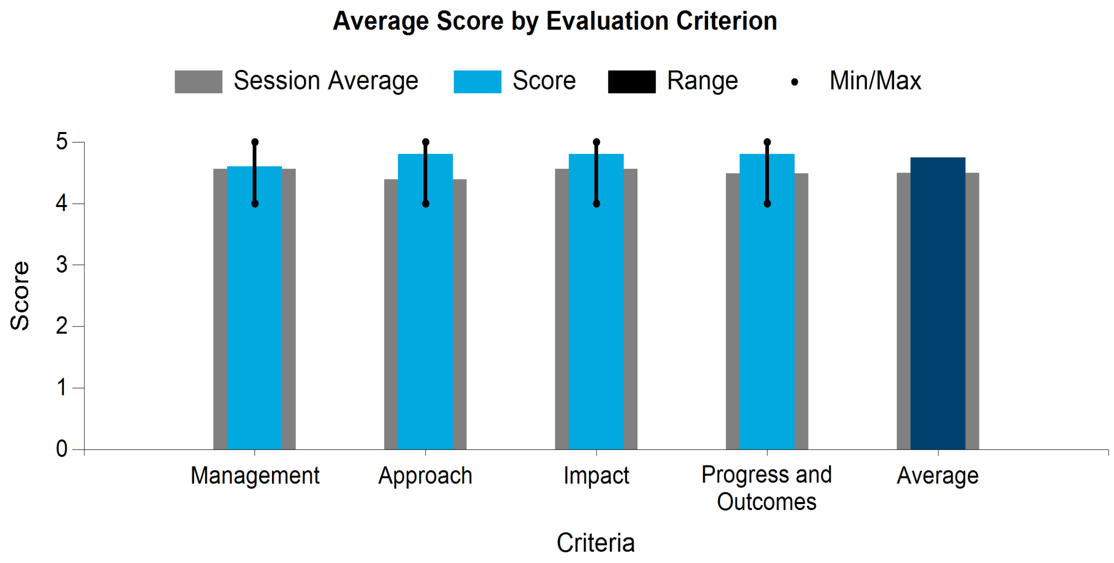
CATALYST DEACTIVATION MITIGATION FOR BIOMASS CONVERSION

Pacific Northwest National Laboratory

PROJECT DESCRIPTION

WBS:	2.5.4.501
Presenter(s):	Huamin Wang; Asanga Padmaperuma; Corinne Drennan
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2022
Total DOE Funding:	$900,000

Catalyst Deactivation Mitigation for Biomass Conversion is addressing catalyst deactivation issues associated with the catalytic conversion of biomass materials. Industrial catalyst lifetimes are on the order of years, whereas catalysts being developed under ChemCatBio may not see TOS beyond 500 hours in early-stage R&D. Some unique qualities of biomass materials bring significant issues to catalyst longevity, which is an overarching challenge. This project, an enabling capability of ChemCatBio, serves as an R&D team specialized in identifying a catalyst deactivation mechanism and developing solutions for improved catalyst lifetime. In the past 2 years, we worked collaboratively and coordinately with various projects to address catalyst deactivation challenges and support specific technologies in expanding catalyst lifetime. Some examples include (1) a comprehensive study on the impact of inorganics on different types of catalyst active sites and mitigation strategies and (2) enhanced understanding of the deactivation mechanism leading to next-generation catalysts with improved stability for ethanol upgrading. We provide fundamental insights into catalyst longevity to guide the rational design of robust and industrially relevant catalyst. We directly address catalysis barriers to improve catalyst lifetime and achieve ChemCatBio's goal of accelerating catalyst development and technology readiness for industry application.



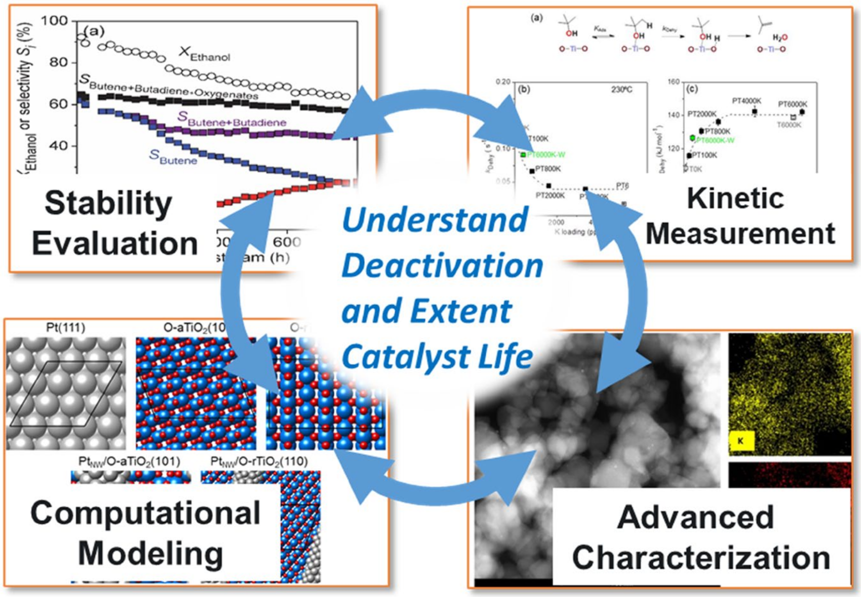


Photo courtesy of PNNL

COMMENTS

- Catalyst deactivation is a key problem that needs to be addressed for every process; it is good to see that at least one project is focused on this problem. It would be good to have a person identified for each portion of the project. Catalyst deactivation mechanisms can be differentiated on the basis of the kinetics of deactivation; some are zeroth order, and some are first order; however, it takes a long time (often 1,000 hours) to obtain enough data to differentiate these. Often there are multiple mechanisms of deactivation. The mechanism that is observed can change with time, which is common for Fischer-Tropsch catalysts, for example, where during the first 100 hours, sintering is key, but when that comes to steady state, coking becomes the most important deactivation mechanism. The faster deactivation is observed first, and a slower deactivation can be observed after the first mechanism has “ended.” Solvent washing is effective; can it be implemented in a commercial system? Does the catalyst have to be removed from the reactor? If so, then it is likely only useful for fluid bed catalysts or maybe where swing reactors are used.

- The team has done an excellent job managing a key, complex issue for catalysis. The management strategy is solid and maintaining good communications with the team and input from the IAB. This is a key to the success of the catalytic program cost improvements and viability, and the program has clear goals and challenges. There is good use of all tools and inputs at hand to address the outlined key issues. There is large potential to impact multiple programs. This is key to success, as indicated for multiple programs, which is why this is so important. There is excellent progress on mitigating deactivation by defining the key areas for the team to focus their efforts.

- Since the 2019 Peer Review, this project has matured considerably and grown into a role as a supporting capability for catalytic upgrading programs. Deactivation is ubiquitous in these systems, and it is a major cost driver and risk factor for scale-up. Having a program dedicated to understanding and mitigating deactivation is critical.

  Management: Interactions and contacts with other consortia and the IAB are clearly defined. The roles of the steering committee and advisory board are clear, and each is contributing to project directions, informing research activities, and ensuring appropriate milestones.

Approach: This project has a pretty targeted focus on increasing catalyst durability, which is a critical challenge in biomass upgrading technologies. The program leverages fundamental catalysis science through collaborations with the ACSC and CCPC to understand deactivation and rationally improve stability. Specifically, the team incorporates appropriate experimental, computational, and characterization techniques to understand the modes and mechanisms of deactivation. The team's mitigation toolbox is robust and considers the relevant aspects of both the prevention of deactivation and the restoration of activity losses. Future direction aims at working with more realistic systems, not only model catalysts, which is appropriate considering that the integration of unit operations always presents a challenge for scale-up.

Impact: This team is helping to improve the lifetimes of catalysts used across ChemCatBio, which is a significant impact. Doing this helps to de-risk technologies and reduce costs for biomass conversion. Two important focus areas for this group are (1) coke deposition and active site poisoning (via potassium) during bio-oil hydrotreating and (2) stabilizing zeolites for use in hot liquid water. These two broad initiatives impact much of the ChemCatBio portfolio in some way, so they are helping to advance the cost-effective production of bio-based fuels and chemicals. It is also worth pointing out that the team is addressing a grand challenge in catalysis science (a fundamental understanding of catalyst deactivation), which is often overlooked in the peer-reviewed literature. Some specific impacts are the development of a stable catalyst for C2 (ethanol) upgrading, understanding the role of potassium ions in the deactivation of Pt/TiO_2, and developing effective regeneration protocols for Pt/TiO_2 catalysts poisoned by potassium when processing dirty CFP feedstocks.

Progress and outcomes: This project has provided support for improving catalyst stability in ethanol-to-butenes technology, identifying coke formation, sintering, and silver oxidation as the main mechanisms of deactivation. This allowed for the development of a better catalyst for the C2 upgrading project. The project was instrumental in determining the mechanism of deactivation by potassium deposition with CFP upgrading catalysts. Understanding the mode of potassium deactivation resulted in the development of a solvent washing method to regenerate material, which has proven effective in improving the catalyst lifetime.

- The key goals of the CDM project are presented on slide 2 and the quad chart (slide 22)—namely, to (1) provide actionable information that leads to catalyst lifetime improvement and (2) enable accelerated catalyst and process development. From the tornado analysis for *ex situ* CFP, upgrading catalysts must last 3 years between change-outs with a regeneration reactor ratio of at least 2:1 to significantly reduce the MFSP below $3/GGE. These are quantitative R&D targets accompanying the goal stated above. The CDM touches every part of ChemCatBio and is highly collaborative. The team should have a dedicated project manager because it touches so many ChemCatBio functions. The key milestone was specific and measured, helping at least two ChemCatBio processes gain insight into the deactivation modes and propose a regeneration technique. This is a reasonable, straightforward milestone to set. Other key deliverables were mentioned on slide 11, such as the impact of steam and hot liquid water, which are so impactful to the bioenergy community. The project risks and success factor were shown on several slides. The risk management plan was not as apparent. CDM supports BETO's Strategic Analysis Goals to ensure high-quality, consistent, reproducible, peer-reviewed analyses; to develop and maintain analytical tools, models, methods, and data sets to advance the understanding of bioenergy and its related impacts; and to convey the results of analytical activities to a wide audience, including DOE management, U.S. Congress, the White House, industry, other researchers, other agencies, and the general public. The CDM project supports the Conversion R&D SMART Goal by 2021, completing the R&D necessary to set the stage for a 2022 verification that produces both fuels and high-value chemicals to enable a biorefinery to achieve a positive return on investment. The project addresses key barriers in Synthesis and Upgrading and Process Integration by identifying impacts of inhibitors and fouling agents on catalytic and processing systems. CDM has a very close interaction across ChemCatBio, with very frequent meetings and interactions with the ChemCatBio steering committee and the IAB. In the case of the CDM, the SOA for providing fundamental insight would be mostly available in the literature or within industrial facilities with plant data. Corporate R&D groups often use a combination of models and proprietary accelerated deactivation techniques. The ChemCatBio team brings the advantage of having access to advanced characterization tools to study the material science related to deactivation events. In that regard, the approach here of deactivation mechanistic elucidation for catalysts on the projects bottlenecked by stability issues should advance the SOA every time. The approach of using advanced characterization and computer modeling is a tried-and-true method for understanding deactivation at the fundamental level. The family of next-generation catalysts resulting from the experimental synthesis, characterization (structure), and performance (function) cycle will be innovative and generate patents and development opportunities with industry partners across ChemCatBio. The catalysis community will benefit greatly from this work because much of it is done in-house by corporate R&D groups to optimize commercial materials. Now, this information will be available to the public, and the CDM understands the impact of their project on the community, which is important. Further, the team has plans on releasing this information in a variety of ways, including the Data Hub. The impact to catalyst manufacturers will be known in future years as the processes are developed using this information in the design basis. Inherently, catalyst deactivation understanding and the generation of new material formulations from this insight has tremendous commercial potential. Although direct industry engagement on the CDM project is not present now, the deliverables will elicit great corporate interest. The CDM team was able to make progress on providing fundamental deactivation insight on upgrading catalysts for two processes: ETO via Ag-ZrO_x/SiO_2 and CFP via Pt/TiO_2. The mitigation approaches were successful for the ETO, and a new-generation Ag-ZrO_x/SiO_2 catalytic material was developed. Metal poisoning by potassium was studied both experimentally and computationally, with fundamental questions remaining on deposition impact. A solvent-based regeneration method was developed as a mitigation strategy. This is excellent progress. The key milestone of helping at least two ChemCatBio processes gain insight into the deactivation modes and propose a regeneration technique was accomplished on time. In fact, for the case of potassium deposition, the risk mitigation action of developing a solvent-based regeneration technique was enacted despite the fundamental questions involving surface deposition still remaining.

- This is an “infrastructure-level” project that is not in the spotlight but is extremely important for the development of catalysts. Such a project deserves more attention. It is impressive to see that the team managed to help the development of quite a few catalysts in the Catalytic Upgrading Technology Area, and it could be beneficial if they can apply their knowledge and tools to the other projects. It could also be beneficial if the team can collaborate with the other teams in the area to develop principles for designing catalysts that can endure long in harsh conditions (such as high-concentration contamination). Considering the diversity of the biomass feedstock, the ability to endure harsh conditions would be important for catalysts.

PI RESPONSE TO REVIEWER COMMENTS

- We greatly appreciate the support for the project, the thoughtful analysis, and the constructive feedback provided by the reviewers. We agree that catalyst deactivation is a key challenge that needs to be addressed for every process in biomass conversion, and having a program dedicated to understanding and mitigating deactivation is critical to the success of ChemCatBio. We will continue to build on the collaborative efforts within ChemCatBio in addressing catalyst deactivation challenges and our early-stage technical successes by (1) maintaining a collective and collaborative approach with core catalysis projects and enabling capabilities for this effort, (2) tackling the most impactful and grand catalyst stability challenges and balance overarching challenges with specific needs of catalysis projects, and (3) utilizing multiple technologies to ensure rigorous deactivation mechanism determination and robust regeneration method development. We agree with the reviewers that understanding long-term catalyst stability is critical to obtaining enough data and capturing the deactivation mechanism change with time. We are working with catalysis projects to evaluate catalyst stability at longer TOS—for instance, 800 hours for the ethanol conversion catalyst—and we are targeting to develop accelerated testing for simulating long-term stability and faster catalyst stability evaluation. We agree with the reviewers that direct industry engagement to access existing plant data and attain great corporate interest in our deliverables is important. We are engaging with our IAB and other industry partners on this topic, and we will provide generated knowledge to industry and catalysis R&D communities via publications, workshops, webinars, and the ChemCatBio Data Hub.

CATALYST DEVELOPMENT FOR SELECTIVE ELECTROCHEMICAL REDUCTION OF CO_2 TO HIGH-VALUE CHEMICAL PRECURSORS WITH OPUS 12

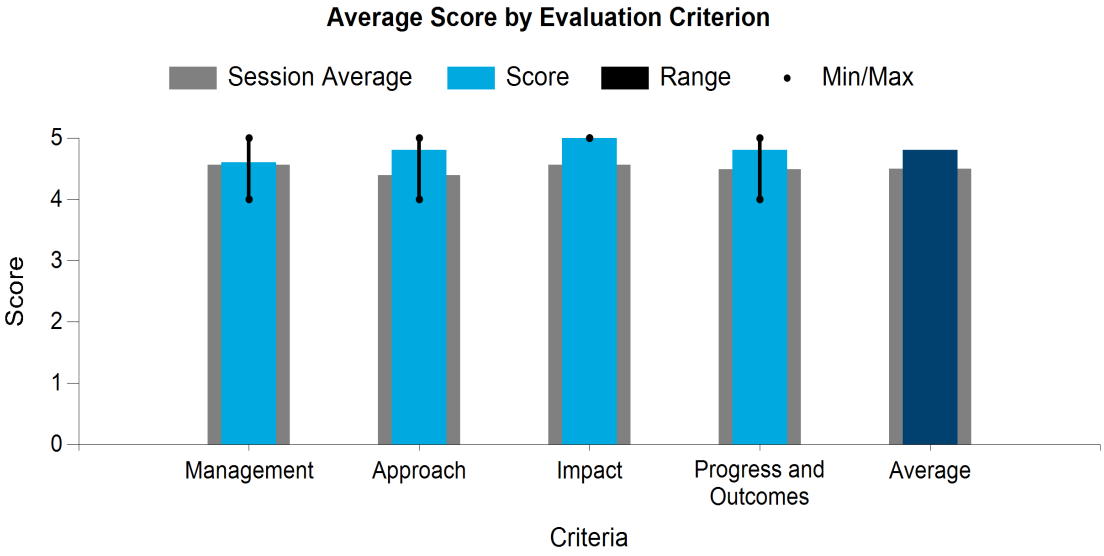
National Renewable Energy Laboratory and Opus 12

PROJECT DESCRIPTION

WBS:	2.5.4.707
Presenter(s):	Adam Bratis; Fred Baddour; Zia Abdullah; Courtney Payne; Jessica Krupa
Project Start Date:	10/01/2020
Planned Project End Date:	09/30/2022
Total DOE Funding:	$614,077

Cost-effective electrochemical reduction of CO_2 (ECO2R) is considered one of the holy grails of green chemistry; however, widespread commercial fuel and chemical production via ECO2R is limited due to the lack of a suitable reactor design and catalysts with high selectivity to the desired products. This technology has the potential to convert CO_2 into a range of molecules that would benefit the biofuels and bioproducts industry. Within the bioenergy industry, more than 45 million metric tons of CO_2 per year are generated from existing domestic biorefineries. With projections of abundant and inexpensive renewable electricity, utilization of this domestically produced CO_2 to make fuels and chemical products has the potential to significantly enhance the economic viability of these operations.

The core innovation developed by Opus 12 is a reactor design that enables ECO2R in a polymer electrolyte membrane (PEM) electrolyzer. A novel polymer blend and transition metal nanoparticle catalyst on carbon in the cathode layer transform a PEM water electrolyzer into a PEM CO_2 electrolyzer. The goal of this project is to enable the scalable synthesis and reactor integration of high-performance nanoparticle catalysts for deployment in a commercial ECO2R system that can convert CO_2 with high selectivity to CO, CH_4, or C2+ products for the specific needs of customer segments within the biofuels and bioproducts industry. Leveraging the synthesis and characterization expertise within ChemCatBio and the advanced PEM diagnostics developed by the Hydrogen and Fuel Cells group at NREL, this project aims to address the explicit industry need of developing scalable, high-performance catalysts to enable the commercialization of tunable PEM CO_2 electrolyzers.



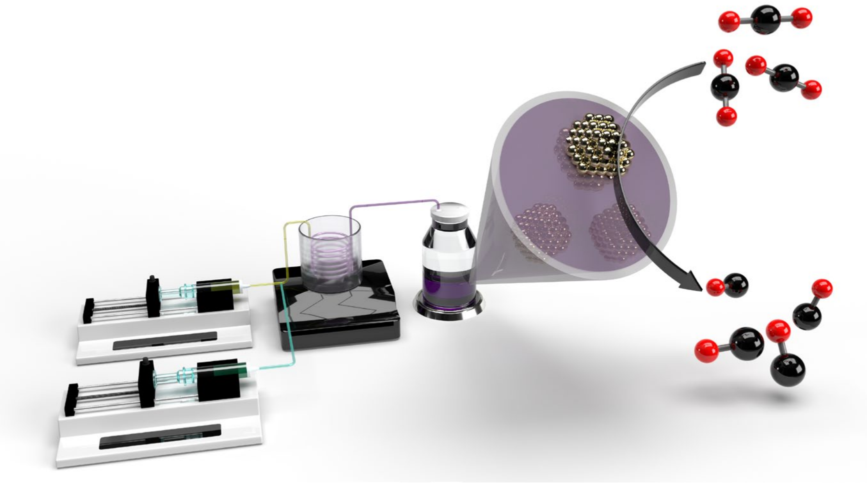


Photo courtesy of NREL/Opus 12

COMMENTS

- CO_2 electrolysis to products is a tall order, with many hurdles. This project attacks one of the key problems of resistance of the cell, often due to poor electrode structure and performance. The team has developed a very generally applicable synthesis procedure for small particle "paints" as well as a clever system to detect pinholes in the electrolytes. The improved life and reduced resistance show that the "engineered" particles are providing real-world value. Opus 12 is lucky to have such a creative and effective partner.

- ECO2R is a clever idea that converts CO_2 to chemicals using abundant power generated by biomass. If achieved, this would significantly reduce CO_2 emissions and increase the economic output of biomass processes. The project advances appropriately and seems to be on its path to achieve the goal.

- The management has done a great job with the program working with their external partner. This program shows the potential of the BETO labs to impact smaller startup companies to attain faster results. My previous concern over this program approach has been unfounded. They are meeting targets in an exciting way, and there is high potential for a unique technology that can become a broad use technology tacked onto existing facilities in industry. A smart approach to CO_2 conversion and the team's joint work has progressed well since the 2019 Peer Review. It could have a solid impact once scaled, and very few proven approaches or options are available to CO_2 conversion. There has been outstanding progress on this program clearly due to the collaborators on both sides. It has great promise for a unique technology approach. I am looking forward to following the progress as they begin to scale.

- The key goal of the Opus 12 project is presented on slide 2 and the quad chart (slide 26) to gain fundamental insight on metal-carbon support interactions within nanoparticle catalysts for carrying out electrochemical CO_2 reduction chemistry enabling scalable synthesis strategies. The project roles are clearly defined between NREL and Opus 12, with some ChemCatBio support from the ACSC and CatCost. No project managers were identified for the team, nor were any quantifiable target KPIs, risks, or mitigation actions given. A key project milestone includes demonstrating a 10% reduction in overpotential and a 10% higher partial current. The project is highly collaborative, giving timely feedback between the partners at each stage in the catalyst design and development cycle. The iterative development approach centers around synthesis and structure-function characterization, which should advance the SOA. The approach was mentioned in the first project overview slide regarding benchmarking the SOA catalysts and subsequent membrane electrode assemblies (MEAs). The project supports BETO's push for novel technologies by pursuing research on innovative technologies that can broadly enable the conversion of feedstock to fuels and products. The approach should result in improved best practices as well as new catalyst materials and MEA fabrication, which allows for the catalyst to be tested in real process environments. This is the actual process-intensified unit. The team understands that very clean sources of CO_2 feedstock are available at biorefineries around the country. The team showed that new synthesis methods can reduce the cost of cathode catalysts in Phase I as well as membrane fabrication quality monitoring. The project clearly has a major impact on Opus 12's business because many of the catalysts screened were not available commercially. The larger impact of CO_2 transformations on the bioenergy industry and DOE was not really discussed. This project is already working with a commercial partner, so the pathway to developing technology-ready hardware is clear. Significant progress toward the project goal of enabling catalyst synthesis through characterization was made meeting particle size and loading targets using aqueous solution synthesis techniques. The photo diode array instrument for membrane quality evaluations was critical to the project. A second-generation catalyst performed much better with stability and efficiency. All of this work was done in batch operational mode. The use of 3D printing, where appropriate, could help reduce fabrication costs. Key future milestones involving overpotential and partial current targets have not been reached. Significant milestones have been achieved with the catalyst synthesis and MEA quality work.

- This seems to be a very good fit for the DFA program. The presentation was clear and cogent, giving a detailed picture of the project organization and technical challenges. I was genuinely excited about the project, which is enabling scalable synthesis and reactor integration of nanoparticle catalysts for deployment in the commercial electrocatalytic reduction of CO_2. The overarching concept is a good one: capturing CO_2 and converting to chemicals and/or fuels, potentially making for a carbon-negative technology. The team is well positioned to capitalize on green, inexpensive electricity as it comes increasingly online.

  Management: This is a partnership between NREL and Opus 12. Their roles are clearly defined, with the synthesis, design, and characterization of catalysts at NREL, appropriately leveraging the ACSC. Opus 12 handles MEA assembly and testing, and NREL does PEM diagnostics. There is a great data management strategy, with respect to proprietary information in particular. Overall, the project management is very good, with appropriate feed-forward/feedback of information to facilitate iterative development.

Approach: The roadmap for this Phase II DFA project is nicely organized. The challenges are clearly identified, which makes for a clear rationalization of the approach. Three challenges are poor uniformity and particle size control in commercial formulations, low loadings of the active phase in the commercial catalyst, and strategies for improved defect detection. The team is using ACSC capabilities to control particle size and heterogeneity. Relevant to technology transfer and scale-up, they have developed a flow technology for catalyst preparation. It uses micro (milli?) fluidics, and I appreciated the use of 3D printing to facilitate rapid prototyping.

Impact: There is a clear impact of improving the economic viability of electrocatalytic CO_2 reduction. Specific to catalysis, providing smaller, more uniform particles for Pt group metals increases active surface area and decreases the cost of a working MEA. The membrane diagnostics tools provide fast detection of failures and insight into failure modes, which is a considerable impact in its own right. It is noteworthy that ChemCatBio has enabled the fundamental evaluation of industrial (electro) catalysts under working conditions, which is atypical for an industrial catalyst.

Progress and outcomes: The team has developed an aqueous solution synthesis method for controlled particle size and a strategy for incorporating catalysts onto membranes. Impressively, this was scaled up by three orders of magnitude. The team has demonstrated that these catalysts can be deposited on membranes without inducing defects. There was a nice integration of the CatCost tool in this project to develop a dollar-per-current efficiency value and select a best catalyst. Detailed advanced characterization identified major challenges in moving the technology forward. This initiated a new round of the development cycle, with synthetic methods designed to address specific challenges. I would consider this an example of closing the loop, which is always nice to see. Second-generation materials showed performance enhancement relative to the first generation, and they are better than a commercial baseline. Importantly, the new catalysts are also stable under working conditions.

PI RESPONSE TO REVIEWER COMMENTS

- We appreciate the reviewers' thorough assessment regarding the goals, scope, and current progress of the project, and we are happy that this project was able to highlight significant progress since the last Project Peer Review. We share the reviewers' optimism and excitement about the potential impact continued work in this area could have on this industry, and we look forward to pushing toward the Phase II goals of the project.

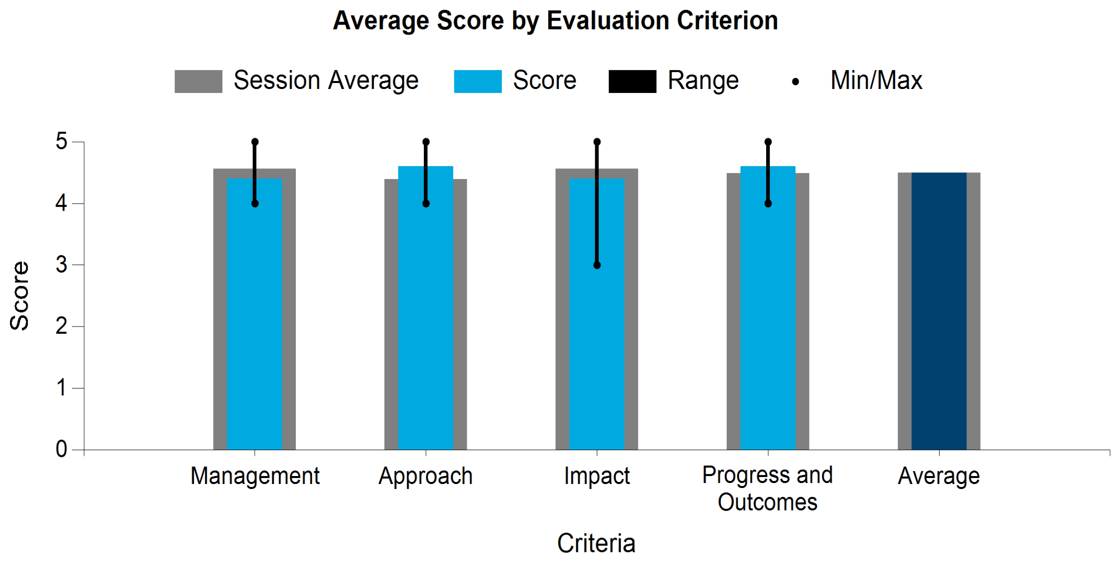
CHEMCATBIO DATA HUB

National Renewable Energy Laboratory

PROJECT DESCRIPTION

WBS:	2.6.2.500
Presenter(s):	Adam Bratis; Kurt Van Allsburg; Zia Abdullah
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2022
Total DOE Funding:	$700,000

The goal of the ChemCatBio Data Hub project is to accelerate the catalyst and process development cycle by developing transformational tools for prediction and collaboration in catalyst R&D. The project is currently focused on the development of the Catalyst Property Database (CPD), a free and public resource released in September 2020. The CPD was designed to advance the SOA for the application of computational data. When computational data, such as computed reaction energetics, are used in catalyst design, they are almost always generated by the researchers seeking to use them, even if similar data have been published previously. One barrier to data reuse that results in this duplication of effort is the difficult process of finding and applying published data, which can be slow, error-prone, and manual. The CPD seeks to overcome these challenges by creating a centralized, searchable database of quality catalyst property data. At present, the CPD contains computed adsorption energies for intermediates along catalytic pathways. During FY 2021 and FY 2022, the development of the CPD continues with a focus on external users and meeting their requirements. A batch upload capability, training and curation procedures, user interviews, and a demonstration of the CPD's utility in accelerating catalyst research are planned. Overall, the Data Hub project and the CPD aim to reduce the time and cost of catalyst research by harnessing the power of data in catalyst discovery.



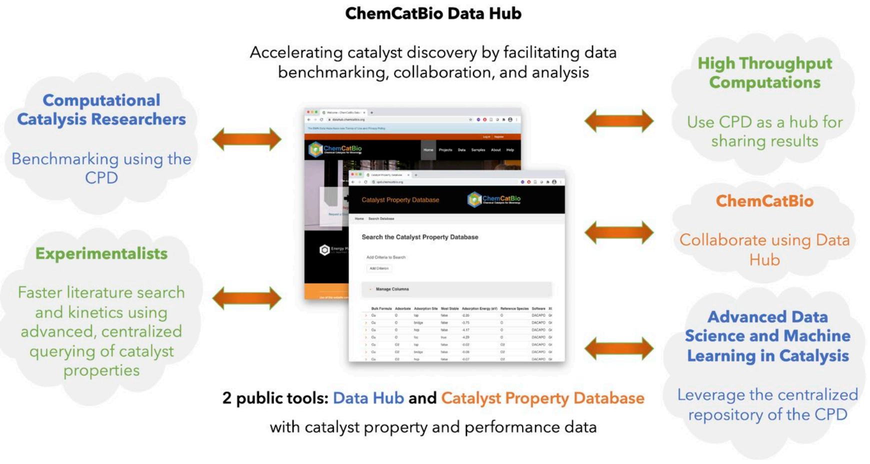


Photo courtesy of NREL

COMMENTS

- The ChemCatBio Data Hub project aims to develop a free and public database for catalysts, the CPD (released in September 2020), that can help accelerate the catalyst and process development cycle. Data are food in the artificial intelligence age. Collecting data has been one of the most important tasks for developing artificial intelligence technologies for catalyst development. The importance of this project is without question. It could be beneficial if (1) the project works with prestigious catalyst-related journals (such as *ACS Catalysis*) or funding agencies (such as DOE BETO), (2) the project uses natural language processing tools to automate or semi-automate the extraction of information from the literature (a similar idea can be found at https://doi.org/10.1021/acs.jcim.6b00207), and (3) the team considers working with the other teams in the catalytic upgrading program to develop catalysts based on these data.

- The concept of having a catalyst database is great. Properly developed, it could save lots of time, effort, and money in catalyst development. One thing I tell my staff is, “The cheapest place to do research is in the library.” Your project is going to make that even more pertinent. I’m glad to see that you are focused on “user-friendly” aspects—that's probably the most significant hurdle to people using any application. Are there links to the original papers from which the data originated? (Answer: Yes.) That is useful to see how the data were obtained and presented—one person’s “yield” is not necessarily the same as another’s, to say nothing of whether they were produced from the same conditions. This would be great if it could be extended to catalyst performance information, which is more useful for applied catalysis. How is the database searchable? It would be great to be able to search for “cobalt-doped zeolite” or “hydrogenation catalyst deactivation” or “ethylene aromatization kinetics.”

- The Data Hub is a crosscutting and enabling capability. The general vision is to leverage data to accelerate catalyst discovery. This project provides a repository for data and an interface for accessing the data. The CPD is informed by the vision for a catalyst design engine, and this project is laying the groundwork (with CatCost) for combining cost and performance into a tool that rationally designs at appropriate cost.

  Management: The project leadership appropriately comprises a diverse group of both theoreticians and experimentalists, which is important to ensuring that the full scope of “catalysis” is represented in steering the Data Hub project. Collaborations with the CCPC and the CatCost team are appropriate and well-leveraged here. Tasks within the Data Hub project are clearly defined, and resources are directed (at relevant scale) toward (1) developing the Data Hub and catalyst property database; and (2) maintenance, security, and oversight. Overall, the management structure is strong. Risks are adequately considered, and mitigation strategies are appropriate. There are no significant weaknesses.

Approach: The architecture described by the team is up to modern standards, and it is appropriate for engaging both casual and power users, a strength of the project. The team outlined an ongoing challenge in the catalyst property database, which is that it intends to increase data quantity by making the database open to public contribution; however, ensuring the quality of those contributions requires robust quality-control measures. The direction of the project to move toward a wiki model that is heavily curated by experts seems good in that it allows contributions of broad data sets while ensuring reliability. In my opinion, this is a good direction because computational results may skew with the models and methods employed, so increasing the diversity of the data available should move the field closer to a "true" value for performance descriptors. The reference species translation feature will go a long way toward standardizing binding energy reporting. The development plan is appropriate and will keep the Data Hub project moving along an appropriate trajectory. There are no significant weaknesses.

Impact: This project removes redundancy in the computational/experimental determination of fundamental catalyst properties. It provides access (potentially) to unpublished data, which is important because they may be of interest beyond the scope of the original publication. This is a huge impact of avoiding individual researchers constantly reproducing a known data set. Ultimately, the CPD may draw from computational and experimental data sources, which should provide reliable benchmarking for, e.g., binding energies and improve uniformity in computational results. The Data Hub addresses market trends that call for new and advanced catalysts and thus connects with numerous targets. There are no significant weaknesses, and this has a great impact for the community.

Progress and outcomes: The overall idea of the CPD is a good one: It is a publicly accessible, searchable repository of catalyst properties. Input data structures have been clearly defined, which will help to standardize the reporting of computational results. The system is in use in its current state and is scalable to support additional data inclusion and utilization. The set of dictionaries and rules for naming conventions will be valuable in standardizing data to improve their accessibility. A straightforward user interface has been created with search and filter tools. It is incredibly easy to use. The CPD has been released to the public. The Data Hub has advanced considerably since the FY 2019 Peer Review, and progress has clearly incorporated feedback from the prior review. The curation of this database is impressive, and I hope to see it continue on this trajectory.

- The goals of the Data Hub project are very clear, as indicated on the quad chart on slide 28 as enabling ChemCatBio and the bioenergy industry to accelerate process development by providing public tools such as the CPD. There is an easy opportunity to apply some measurable and time-bound aspects to this goal. The project credentials and experience of the team seem quite reasonable. The roles of the team members were not clearly defined, and the project manager was not identified. The team clearly stated the critical two tasks (Data Hub/CPD and project management), the risks associated with them, and the corresponding mitigation actions, including project creep, Data Hub efficacy, user-friendliness, and data quality. Much of the mitigation approaches involve user feedback and engagement as well as training. The key end-of-project milestones and targets were provided on the quad chart—namely, CPD demonstration and case study validation showing at least twice the time savings. Other KPIs and/or metrics associated with tracking the progress of this work were not mentioned. The communication plan for the Data Hub was not explicitly stated. As indicated on slide 10, two project collaborations are ongoing with the CatCost tool and the CCPC. No formal advisory board or academic or industry engagement is present at this stage. The user feedback is present only as mitigating actions. Subject matter expert interviews will take place at the FY 2021 go/no-go stage.

  In terms of the SOA for public, web-based, online comprehensive databases for catalytic materials (e.g., DOE Data Explorer, Open Energy Data Initiative Data Lake, Open EI, Materials Cloud Archive, ioChem-BD, PubChem, COD, NOMAD, NIST suite of Standard Reference Data: 3, 40, 69, 101, 103b, 141, 150, 203), the CPD-focused initiative is poised to push new actionable information out to the scientific community and complement existing databases. This will be the first of its kind, and the information will be uniquely suited for stakeholders involved in the design of heterogenous catalysts and processes for the bioenergy community. Additionally, the level of user engagement appears to be enhanced relative to other public data repositories and not simple storage/file sharing functionality. The CPD design and architecture appear to be reasonable and robust, and the team seems to understand the importance and need for high data quality. This work supports the BETO Strategic Analysis Goals to ensure high-quality, consistent, reproducible, peer-reviewed analyses; to develop and maintain analytical tools, models, methods, and data sets to advance the understanding of bioenergy and its related impacts; and to convey the results of analytic activities to a wide audience, including DOE management, U.S. Congress, the White House, industry, other researchers, other agencies, and the general public.

The approach of establishing a data repository for ChemCatBio is not necessarily the most innovative. It is required and essential for modern science, especially if ChemCatBio ever wants to leverage learning algorithms to help accelerate catalyst design. The art of creating species translators of high data quality is very innovative. It's exciting to see how that feature will fill in the data gaps in the future. The issue of translating to liquid-phase data will continue to be a challenge for this work. The Data Hub team understands the importance of the CPD on the catalysis community by limiting the redundant experimental effort. On the other hand, consensus and redundancy can often be used as an important data quality tool, especially when conducted within interlaboratory coordinated testing campaigns, which, in this case, is the published peer-reviewed literature. The predictability aspects of the CPD with respect to fundamental reactivity descriptors hopefully will incorporate the physical material constraints, thus pointing to realistic opportunities unforeseen by practicing catalysis scientists. In other words, suggesting realistic materials that can be synthesized with existing precursors and economic techniques will be important. This is important work and should include an education/training campaign in conjunction to realize the full impact. The CPD was released to the public in September 2020, which is a key accomplishment and proof of the commercial impact. Within a year, the CPD was released to the public. This was significant progress toward the project goal of enabling ChemCatBio to achieve its mission of accelerating the catalyst and process development cycle by providing public tools such as the CPD. The focus of the team on the critical goals should be rewarded and acknowledged. The work effort presented here has not been diluted by competing tasks and objectives, although there are clearly other initiatives taking place. This deliberate focus will need to continue as the prediction capabilities in the CPD as well as the translation tasks must be further developed to create the design acceleration potential. Key milestones were accomplished in the areas of data structure and SQL development, standardization on naming rules, and the query interface. Now that the infrastructure is in place, the use of automation scripts via Python is anticipated for uploading and data preprocessing, and bulk importing was mentioned directly. With the Python script, they are trying to address the automation and data quality for teasing out the accuracy and to manage the metadata. The team is working on more visualizations and analysis tools. All of the key milestones were reached on time.

- The management team has made outstanding progress considering the complex task to provide a relevant and usable database to avoid duplication and nonrelevant information. There is no issue with the approach, which is clearly a grand challenge considering the massive amount of data generated by the teams during the past years and going forward. In the past year, the Data Hub project was viewed as critical for the catalyst speed of development, and the team has responded to develop this database for use by all catalyst team members and for public use to be implemented this year. I view this as critical to speeding the catalyst development timeline to commercial use and reduced cost to make renewable fuels/chemicals a viable option via the key feedstocks, and it could be a way to engage more chemical companies and fuel companies because the team built a great way for them to access the information, reapply it, and perhaps even provide impetus for further direct engagement with catalyst teams. The progress and outcome were sufficient with the limited funding applied early in the program. My own experience teaches that there is too much reinventing the wheel if there is not a good way to search and define previous work results that are solid to avoid duplication of effort.

PI RESPONSE TO REVIEWER COMMENTS

- We thank the reviewers for their thoughtful comments on our project direction and management. In general, the reviewers found the project goals to be clear and appropriate to the data needs of the catalysis community. In particular, the reviewers noted the value of reducing redundancy in catalysis research and of unique features like the proposed reference species translation capability for the CPD. They further highlighted the growing importance of data in research as well as the value of a resource that can facilitate benchmarking and reactivity descriptor discovery by providing a central, searchable repository for large quantities of data. We were glad to hear broad support of these development directions, and we will keep these priorities in mind as we continue development. The reviewers also provided a number of helpful suggestions to guide the project. They highlighted the importance of an education and training campaign to ensure that the CPD is usable across the catalysis research community, which aligns with the FY 2021 Q3 milestone for this project, "Develop Documentation, Training, and Curation Procedures." It was noted that computational results can become skewed if they represent only a few research groups, methods, etc.; to mitigate this risk, our outreach efforts will aim for diverse and representative coverage when recruiting new data contributors. Toward the goal of data growth, the reviewers suggested working with catalysis journals and funding agencies to encourage or require uploads of data to relevant databases such as the CPD. They also suggested using natural language processing tools for mining data from existing literature and targeted collaborations with other teams in the catalytic upgrading program. We are evaluating each of these approaches and agree that they are promising avenues for accelerated data growth. The reviewers suggested new types of data sets, such as catalyst performance data, and additional metadata for existing data sets, such as keywords focused on the related catalytic process application. These opportunities to expand the database content would increase the database utility and will be considered with future development efforts. As a point of clarification in response to a question about the project management, the project is performed at NREL and led by Kurt Van Allsburg as PI (Carrie Farberow pre-FY 2021), with Trevor Smith as the BETO technology manager (Andrea Bailey pre-FY 2021). In conclusion, the reviewers noted that the project has advanced substantially since the 2019 Peer Review and has demonstrated focused progress despite a number of competing priorities. We appreciate this assessment and the reviewers' numerous helpful comments, which we will integrate into project plans as we continue the development of data tools to accelerate catalysis research.

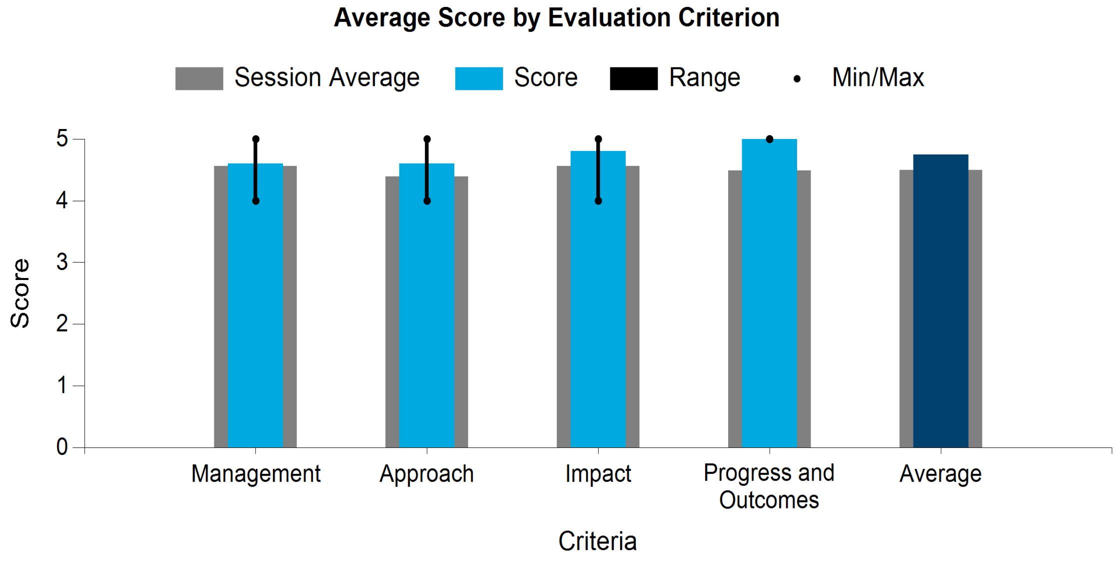
OVERVIEW OF CHEMICAL CATALYSIS FOR BIOENERGY CONSORTIUM

National Renewable Energy Laboratory

PROJECT DESCRIPTION

WBS:	2.6.3.500
Presenter(s):	Adam Bratis; Josh Schaidle; Zia Abdullah
Project Start Date:	10/01/2019
Planned Project End Date:	09/30/2022
Total DOE Funding:	$620,000

Catalysis plays a central role in converting biomass and carbon-rich waste feedstocks into fuels and chemicals; however, critical catalysis challenges exist that are limiting the commercialization of emerging bioenergy technologies. By leveraging unique DOE national laboratory capabilities and expertise, ChemCatBio seeks to overcome these catalysis challenges and accelerate the catalyst and process development cycle. The foundation of the consortium consists of an integrated and collaborative portfolio of catalytic technologies and enabling capabilities, which positions ChemCatBio to address both technology-specific and overarching catalysis challenges across the development cycle from discovery to scale-up. The core catalysis projects target technological advancements for specific conversion processes, such as the catalytic upgrading of biochemical process intermediates, CFP, C1 and C2 upgrading, and electrochemical CO_2 reduction; and the enabling technologies provide access to world-class capabilities and expertise in computational modeling, materials synthesis, advanced *in situ* and *in operando* catalyst characterization, and catalyst design tools.



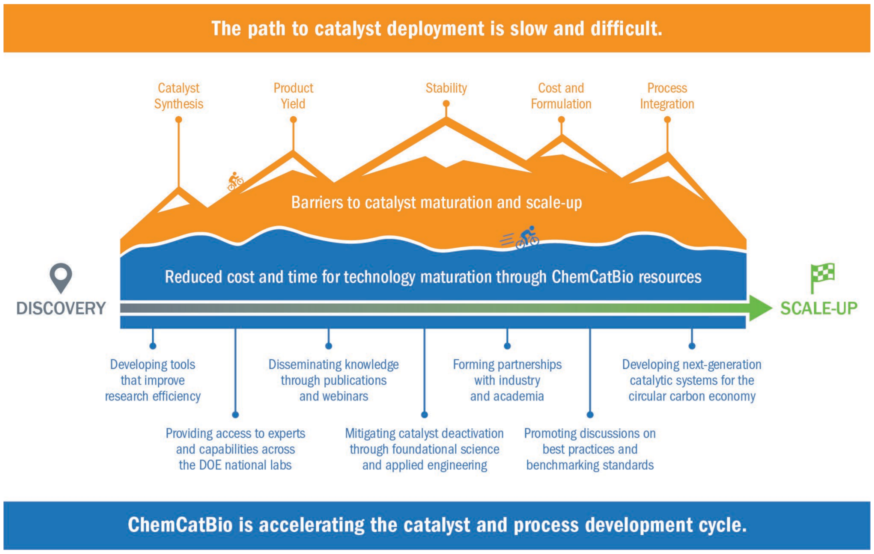


Photo courtesy of NREL

COMMENTS

- ChemCatBio provides a unique platform that enables researchers to accelerate the development of catalysts and relevant technologies for bioenergy applications. This unique platform gathers researchers with a wide variety of backgrounds and expertise, creating the opportunity for interdisciplinary research. It would be beneficial to create a mechanism that makes everyone's voice heard, especially for such a large group of researchers. It could also benefit if we could use tools such as Teams and Zoom that could enable "virtual" meetings and discussion. Such tools may change the way we do research even after the pandemic. The research of ChemCatBio shows significant advancement in the last 2 years and is on its path toward the DOE BETO goal of affordable bio-based fuel. This research would fundamentally impact society. It could be beneficial if the research could leverage more power of artificial intelligence, computation, and advanced characteristics. Indeed, some technologies themselves are still in the early stage, such as machine learning, though they are advancing rapidly. It could be useful if they can be integrated into the research of ChemCatBio more closely.

- The management team is well organized and does an outstanding job handling the complex number of interactions (more than 130 people involved). Josh Schaidle has a big responsibility and is doing a great job. The cross-communication within teams and the overall management group is outstanding. The IAB is solid, with a revamp from the previous board; the industry partnerships are broad-based; and the responsiveness to the IAB feedback also indicates management flexibility to shift based on issues and recommendations. Interviewing industry experts is an excellent addition as well. I see only one minor issue that is missing from the entire catalyst team development: Low-temperature metathesis is now broader than pharma today, and I would have liked to see some FOA or program that involves the latest in metathesis catalyst development applied to some of the upgrading programs of the intermediates. Again, this is a minor issue, in my opinion, as the results speak for the team's effort in foundational science and applied engineering as key to rapid catalyst development as well as shifting to realistic feed streams. The impact is clear, as shown within the individual project progression, the acceleration noted from past reviews, and better definition and action to close out projects if they are not able to attain their goals. I view catalysis as the most important part of the BETO programs to reach the desired $3/GGE, which is a huge challenge in today's economy of petroleum fuels. There is an amazing number of scientific publications, which is a key part of the BETO program to get the catalyst science out there to the experts in industry and academia. There are no issues with the progress and potential outcomes going forward, as catalysis is so critical to the programs. This work has proven itself, as several players are engaged now through licensing their technologies. I see this team's ability to impact both biofuels and the chemical industry in the future. Catalysis is critical to providing enhanced productivity, cost, and selectivity to products and yield needed to achieve the lofty goal of $3/GGE. I see the acceleration resulting from the reorganization and quick decision-making based on better criteria, targets in catalyst development, and the feedback mechanisms established by the team to accelerate progress on catalyst development.

- Management: The management of ChemCatBio is clearly outlined. There is a hierarchical structure that centralizes the POCs and streamlines input from various advisors and stakeholders, both internal to BETO and external in academia and/or industry. Importantly, the team relies on their IAB to help direct research toward impactful areas. The ChemCatBio program appropriately leverages input from a steering committee, and the roles of individual members are clearly defined, ensuring leaders take ownership of the various action items required for success of the program. These include coordination of meetings, outreach to industry, liaisons with other consortia, and POCs to lead specific initiatives. The team's public outreach effort is centralized with a web interface. The overall vision is one of a very collaborative portfolio of projects that cover core technologies, enabling capabilities, and industry partnerships. Crosscutting support is necessary and appropriate to tackling the complexity of biomass upgrading. The portfolio has been updated to reflect sunsetting projects, feedback from the IAB, feedback from the 2019 Peer Review, and/or internal R&D. Programmatic changes are appropriate responses, and they are steering the program in a positive direction. Consolidation of programs into C1/C2/electrochemical should help to streamline efforts directed to common applications. There are no significant weaknesses.

  Approach: The overarching focus of the program is to accelerate catalyst design, development, and commercial adoption, ultimately reducing the cost and time for technology maturation. Broadly speaking, the program covers all the necessary bases (design, synthesis, characterization, testing, theory, deactivation, economic analysis, scale-up, etc.) quite well. This is all aimed at reducing risk in the production of biofuel and bioproducts. There are no significant weaknesses.

  Impact: The program has demonstrated multiple important outcomes. Publications, presentations, and patents are adequate in number, and the work they detail is high quality. The CatCost tool and the CPD are both outstanding, publicly accessible tools. The ChemCatBio intellectual property portfolio has resulted in numerous licenses, clearly showing commercial relevance. Three DFA projects have successfully transitioned from Phase I to Phase II, which is important for supporting the commercial deployment of next-generation bio-based fuels and products.

  Progress: There has been an appropriate focus on catalyst stability, which is a longstanding challenge in biomass upgrading. This is particularly true for thermochemical processes like pyrolysis oil upgrading, where inorganics and coke formation shorten catalyst lifetimes. This program has generated fundamental understanding of deactivation mechanisms, leading to mitigation strategies and better regeneration protocols. The CatCost tool has expanded capabilities to make outputs more informative and robust, as well as to streamline user interface. The CPD is an outstanding tool that will be of broad interest to those doing fundamental catalysis research in design and/or kinetic analysis. Binding energies are a critical predictor of catalyst performance, yet, historically, they are accessible only via density functional theory or challenging surface science experiments. Having this centralized repository is extremely useful to the field. Cross-consortia collaborations were highlighted appropriately. These are important in that they interface ChemCatBio programs with separations, Co-Optima, lignin upgrading, and scale-up and integration, etc., which cover important parts of biomass upgrading technologies that are external to the catalysis focus here. There are no significant weaknesses.

- The goals of ChemCatBio are very clear, as indicated on the quad chart on slide 25 as enabling ChemCatBio to achieve its mission through leadership and management. There is an easy opportunity to apply some measurable and time-bound aspects to this goal. The project team also provided a mission and vision on slide 2 of accelerating catalyst and process development, which helps further clarify the purpose. The single POC management model keeps the quality of the messaging from the consortium consistent and clear. It also has risks associated with it being a single-point bottleneck if the director is unavailable for some reason. These risks were not discussed as much. The director serves as the de facto portfolio manager and has proven the ability to act on results and feedback by enacting several reorganization campaigns. The key end-of-project milestones and targets were provided on the quad chart—namely, the Catalyst Design Engine, CatCost, and deactivation and feedback corrective actions. The portfolio KPIs and/or metrics associated with this work were not provided. The communication plan for ChemCatBio is thorough and extensive. As indicated on slide 6, vertical communication with BETO takes place frequently. The steering committee meets regularly, engaging industry and academia stakeholders in both face-to-face meetings and other teleconferences. The roles are clearly defined with adequate manpower. Quarterly teleconferences are taking place with the IAB.

In terms of the SOA for the DOE BETO consortia (e.g., Bioprocessing Separations Consortium, Agile BioFoundry, FCIC, and CCPC), ChemCatBio continues to be a stand-alone, unique effort, with a vision often found only in premier industrial catalyst manufacturing corporate organizations, especially with access to such advanced tools and professionals. The number of teams involved alone sets it apart, and the program continues to advance work that supports BETO and the technology area mission of developing and demonstrating transformative and revolutionary bioenergy technologies for a sustainable nation as well as the BETO goals to develop commercially viable bioenergy and bioproduct technologies. ChemCatBio has an opportunity to strengthen the support of the Conversion Technology Area objectives pertaining to integrated conversion technologies by showing how new catalyst materials are moved into other BETO scaled-up system integration efforts. ChemCatBio does an excellent job of supporting the EERE Strategic Plan goal of enabling a high-performing, results-driven culture through effective management. The BETO Strategic Analysis Goals to develop commercially viable bioenergy and bioproduct technologies to enable the sustainable, nationwide production of biofuels are supported well in the ChemCatBio initiative—as are the Strategic Analysis Goals to ensure high-quality, consistent, reproducible, peer-reviewed analyses; to develop and maintain analytical tools, models, methods, and data sets to advance the understanding of bioenergy and its related impacts; and to convey the results of analytical activities to a wide audience, including DOE management, U.S. Congress, the White House, industry, other researchers, other agencies, and the general public. ChemCatBio supports the Conversion R&D SMART Goal by 2021, completing the R&D necessary to set the stage for a 2022 verification that produces both fuels and high-value chemicals to enable a biorefinery to achieve a positive return on investment. The project addresses several key barriers in Synthesis and Upgrading—Ct-H. Efficient Catalytic Upgrading of Sugars/Aromatics, Gaseous and Bio-Oil Intermediates to Fuels and Chemicals, and Integration and Intensification Challenges—Ct-J. Process Integration (2) identifying impacts of inhibitors and fouling agents on catalytic and processing systems. In support of the Synthesis of Intermediates and Upgrading initiatives, ChemCatBio is supporting the upgrading of bio-oils and syngas within the Chemical Conversion to Intermediates and Products as well as strengthening the Enabling Tools within the Computational Modeling & Analytical Tools and Standards & Method Development efforts.

Finally, ChemCatBio supports BETO's push for novel technologies by pursuing research on innovative technologies that can broadly enable the conversion of feedstock to fuels and products such as the electrochemical CO_2 work. The approach of rationally designing catalyst surfaces and validating the hypothesis with characterization tools is a plausible, accepted practice within microscale catalysis. The incorporation of tools that allow for larger multiscale analysis and validation is more innovative. The approach is based on sound premise that throughout human history tools have enabled and accelerated innovation. The development of the CatCost tool is one example in this project. Other key enabling tools (e.g., HTS, pilot-scale reactor banks with industry partners) contributing to the accelerator function in ChemCatBio should be further clarified and well defined along with the proper metrics. The project team views data availability as a way of accelerating by getting key information to the fingertips of the end user. The other way is to leverage the existing catalyst library of materials. The CPD is another way to measure to the acceleration. ChemCatBio realizes that it can serve as a major public knowledge hub for BETO on all things related to bioenergy catalysis. Further, ChemCatBio has the management mechanisms in place to match industry needs with national lab resources. The academic community also serves a key role in helping to accelerate knowledge in catalysis through publication and student development. ChemCatBio has an opportunity to influence this process as well in terms of future workforce development. ChemCatBio has already licensed three technologies that involve fuel production and advanced catalyst synthesis, so the commercial potential of the project has already been realized. Further, the public tools have been widely utilized and accepted, and industry partners have provided solid testimonials. The commercial pathway to catalyst development and manufacturing has not been as clear, yet advancing the time for material development is the core of the program. There was some progress toward the project goal of enabling ChemCatBio to achieve its mission of accelerating the catalyst and process development cycle through leadership. There were interesting deactivation study results for ethanol upgrading and CFP catalysts. These results should immediately connect back to the acceleration and show the positive impact to the process development cycle. The public CatCost tool continues to excel in development functionality and features. The new property database tool has been made publicly available. Both of these efforts demonstrate ChemCatBio's leadership in facilitating catalyst development as well as the IAB membership revamp. Most of the key end-of-project milestones have already been reached ahead of schedule or have significant work completed on them—namely, CatCost tool development, the CPD in support of the Catalyst Design Engine, engagement of Bioprocessing Separations Consortium on BDO upgrading via membrane work, acid upgrading to diesel with Co-Optima, and the CFP scale-up with the CCPC. The initial key project milestone timeline was not presented to establish the schedule savings metric and to give timing to share the website content on catalyst deactivation studies.

- This is a well-structured program that solicits input from across the spectrum of stakeholders of the catalysis community. Active portfolio management is an important feature that helps the program remain relevant to current, shifting trends. A focus on products that cannot be provided by other types of tech—e.g., solar or electrochemical—focuses the efforts where they can make the most difference in the near and long term. It is good to see that TEA is highlighted and is used to inform the targets for various processes. The technology licenses and patents are a positive, tangible measure of the success of the program. One missing aspect is longer life testing of catalysts, i.e., >1,000 hours. Although 100 hours is nice, many processes do not reach steady state until a much longer time. Also, different mechanisms of deactivation have different "run-in" periods before they make a significant (even measurable) impact.

PI RESPONSE TO REVIEWER COMMENTS

- We would like to express our appreciation to the reviewers for taking the time to participate in BETO's 2021 Peer Review and for their thoughtful analysis and constructive feedback on ChemCatBio. Building on our progress to date, we will use the reviewers' feedback to guide our work in the coming years, especially in the areas of (1) defining KPIs/metrics for the consortium, (2) enabling the technology transition toward scale-up and integration within the BETO program, (3) developing and leveraging tools (e.g., artificial intelligence, high-throughput synthesis/testing, and durability testing rigs) that facilitate further acceleration of the catalyst and process development cycle, (4) supporting effective collaboration and communication mechanisms that enable every person within the consortium to have a voice and to be heard, and (5) expanding and extending catalyst durability tests to accurately identify deactivation mechanisms that may plague commercial operation.

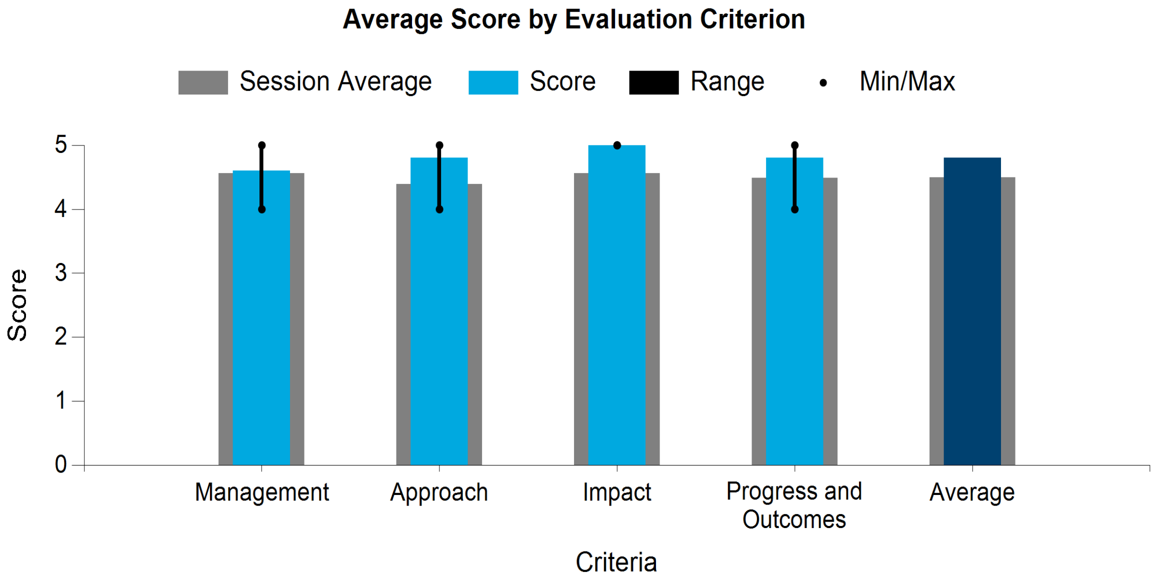
ENABLING COMPLEX BIOMASS FEEDSTOCK FOR BIOPOWER COMBUSTION AND AUTOTHERMAL PYROLYSIS

Oak Ridge National Laboratory, National Renewable Energy Laboratory, National Energy Technology Laboratory, and various industry partners

PROJECT DESCRIPTION

WBS:	5.1.2.102
Presenter(s):	Jim Parks; Tim Theiss; Zia Abdullah
Project Start Date:	10/31/2018
Planned Project End Date:	03/31/2021
Total DOE Funding:	$1,500,000

This project addresses the challenges of utilizing biomass and related waste feedstocks for the production of electricity (power) by utilizing a computational approach. The project team consists of ORNL, NREL, NETL, Iowa State University (ISU), and industry and municipality partners. The complexity and variability of feedstocks and the implications for gasification and combustion processes are captured with mesoscale particle models and in process-scale reactor models. The resulting models capture critical parameters to enable improved reactor design and optimal controls for more efficient and cost-effective biopower generation. The research also addresses the holistic energy system in the United States because (1) the model tool set is applicable to autothermal conversion processes for fuel production from biomass; and (2) the models enable the valuation of byproducts from biomass-to-fuel processes for electricity production, which has an overarching impact on the economics of both biomass-to-fuel and biomass-to-electricity renewable energy pathways.



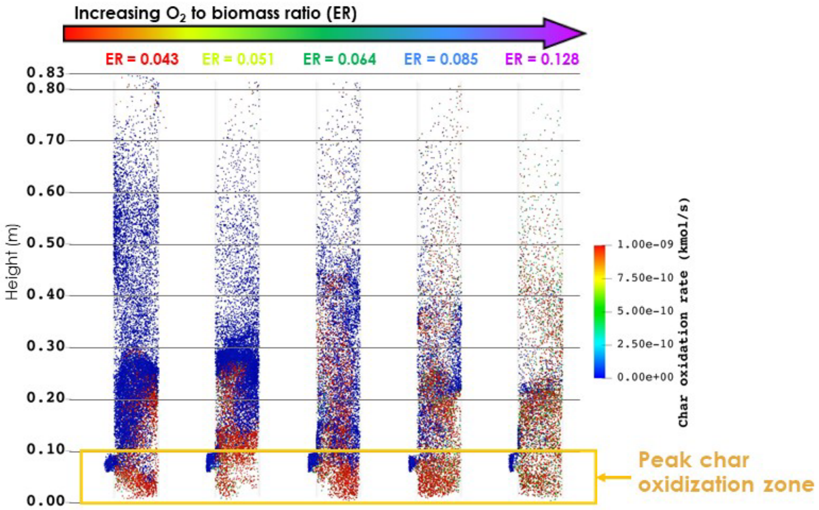


Photo courtesy of ORNL/NREL/NETL/various industry partners

COMMENTS

- This is a creative combination of combustion and partial oxidation to study key common features of the two processes. The biomass injection must generally keep the biomass <200°C to prevent premature pyrolysis from producing oils that clog the inlet. The biomass will need to heat from the inlet temperature to the reaction temperature. Does char oxidize faster than the biomass pyrolysis products (likely no)? The H_2/CO ratio is already poor with pyrolysis; wouldn't it be worse with O_2? Would it make sense to allow the pyrolysis to produce char, collect it (with the catalyst, if present), and feed a portion of it (the rest can be sent to waste to remove the metals) with O_2, but separate from the biomass, to get pure char oxidation? Then the heat can be used to drive the pyrolysis. On slide 21, showing where the entry of the biomass is varied, what is happening below the injection point? Where are the materials from the cyclone injected?

- I thought this was a great project, with a lot of heavy lifting in reaction engineering and meso- and macroscale modeling to enable reactor design and process control. It is becoming rare to see this kind of work in the catalysis and reaction engineering community these days, but the impact on scale-up is undeniable considering that most industrial-scale reactors are at least partially controlled by heat and mass transfer and very likely deviate from ideal packed or fluidized bed models. This team showed very nice results from multiphysics simulations to model real reactor performance; this seems like a critical need for moving these technologies to larger scales. Overall, the results we saw focused on biopower with additional support for biomass to fuels, but the techniques are applicable anywhere.

  Management: The scope of the project is clearly outlined, and there are focus areas on biomass to electricity and biomass to fuels. The former is a collaboration on biomass combustion between CanmetENERGY and NETL, and the latter is a collaboration on autothermal pyrolysis in fluidized beds between NREL and ISU. Overall, the project is well managed.

  Approach: The team uses a multiscale approach including atomistic simulations for intrinsic catalyst properties; mesoscale finite element method simulations of transport phenomena; and full-scale reactor simulations using multiphysics packages (CFD).

Impact: A key impact of this project is that these thermal and thermochemical conversion processes are too complex to adequately treat with simple reactor models. It is unlikely they adhere to ideal flow patterns, and they are almost certainly constrained by rates of heat and mass transfer. The best way to anticipate their performance is with multiphysics simulations, so it is nice to see that the team is making them sufficiently tractable to put into routine practice and build insight about these systems.

Progress and outcomes: Work in the biomass-to-electricity project has revealed optimal particle sizes for fluidized bed combustors. Impressively, the team can access online data from a working 50-kW combustor, which shows good agreement with full-scale models and serves as an important validation of the methodology. The work in autothermal pyrolysis is well motivated, and the particle-scale models developed by the team highlight the significant impacts of temperature and composition gradients in solid particles undergoing pyrolysis. Analogous to the comment regarding combustion, the team has experimental validation of pyrolyzer models through its collaboration with ISU, and one observes good agreement between the models and experiments. Having these multiscale insights into reactor performance is incredibly powerful, and I see this as an important step in de-risking technologies as they move from the laboratory to pilot and demonstration scales.

- Team collaboration for the two project areas appears smooth and without issues. The modeling approach is sound. There is a clear impact on the two programs: power and fuel. The modeling team, as always, is doing an outstanding job to assist programs, and there is no exception for these projects. The team demonstrated the true power of modeling in this program to have future impact.
- The key goal of the biopower project is presented on the quad chart (slide 24) to develop models to improve reactor design and control. The measurement for this goal was not explicitly mentioned, and it is assumed to be metrics such as standard error of prediction or correlation and validation agreement criteria. The multiscale project is wrapping up this year and centers around the CFD modeling of the CanmetENERGY fluidized 50-kWt combustor and the AT-Py unit at ISU. There was not much information available concerning the management plan. No information was provided specifically on the communication plan. The project partners are an impressive industrial-national lab group all focused on operating real equipment at scale. The multiscale CFD approach presented here to model two independent units before a process integration design campaign is the proper technique and should definitely result in advancing the SOA of reactor modeling for both biocombustors and AT-Py units at a large scale. This information is just not readily available or even accessible for process development teams working at large scales. The type of commercial partners involved in this project should advance work that supports BETO and the technology area mission of developing and demonstrating transformative and revolutionary bioenergy technologies for a sustainable nation as well as the BETO goals to develop commercially viable bioenergy and bioproduct technologies. In the future, this work can easily pivot to CFP systems, which will advance and support the Biochemical Conversion Program objectives pertaining to integrated conversion technologies by showing how new catalyst materials are moved into other BETO scaled-up system integration efforts. The project will advance the Strategic Analysis Goals to ensure high-quality, consistent, reproducible, peer-reviewed analyses; to develop and maintain analytical tools, models, methods, and data sets to advance the understanding of bioenergy and its related impacts; and to convey the results of analytical activities to a wide audience, including DOE management, U.S. Congress, the White House, industry, other researchers, other agencies, and the general public. The project supports and advances the Conversion R&D SMART Goal by 2021, completing the R&D necessary to set the stage for a 2022 verification that produces both fuels and high-value chemicals to enable a biorefinery to achieve a positive return on investment. In support of the Synthesis of Intermediates and Upgrading initiatives, this work is strengthening the Enabling Tools within the Computational Modeling & Analytical Tools as well as the Standards & Method Development efforts. Of course, the approach of using CFD and FEA modeling to make front-end design decisions is not considered new or innovative. It is necessary for high-quality process design engineering, and this work will lead to innovative configurations/operation schemes when the integration takes place in the

future. The incorporation of the mesoscale model brings even more innovation to this work. The team understands how this work can directly impact the two 50-ton/day demonstration AT-Py plants being commissioned this year and next year. If the data from all of the pilot-scale work are reexamined and modeled along with data from these demonstration facilities, this will resonate in a huge way across the bioenergy community. The project comprises industry partners that can use this modeling information immediately for their projects. The team provided a clear understanding of degradation and oxidation chemical dynamics within the various riser zones, creating a particle-based char oxidation model showing the impact of geometry and intra-particle char formation profiles. The team showed a validated 3D model for lab-scale AT-Py experiments. The pilot-scale model of the ISU unit was developed using the DOE MFiX code showing the impact of the equivalence ratio of char oxidation in the riser and bio-oil yield. These were all good modeling efforts toward the overall project goals. Key end-of-project milestones have been reached on time—namely, the particle-scale model looking at air-to-fuel ratio effects, CFD models of fluidized combustors, and validated lab-scale models. The nitrogen oxide (NO_x) work and full-scale model validation work are the only outstanding milestones, which seems quite achievable for this team within the project time frame.

- This project is another example showing how computation can contribute to the development of bioenergy processes. The research enables the visualization and quantification of spatial locations of pyrolysis, volatile oxidation, and char oxidation processes for biomass to electrons. It also helps to capture char oxidation effects at both the particle and reactor scales, thereby enabling the capture of feedstock effects on autothermal biomass-to-fuel processes. Such information would be very hard to catch in the experiment. The team collaborates closely with their experimental colleagues, enabling a tight connection between computation and experiment. It would be beneficial if the team can leverage the ability of computation to explore more operating conditions for the process.

PI RESPONSE TO REVIEWER COMMENTS

- The CCPC and ISU thank the reviewers for the feedback on our computational science R&D supporting biopower and autothermal pyrolysis. We are pleased to see that the majority of the feedback comments were positive in nature, and we also appreciate the outstanding comments citing the impact of the R&D. Regarding the comment on the metrics for model accuracy, we are comparing the model results to experimental validation data sets, and in the forthcoming publications from the project, we will provide quantitative comparisons between the model and experimental results.

  Regarding the comment "The team understands how this work can directly impact the two 50-ton/day demonstration AT-Py plants being commissioned this year and next year. If the data from all of the pilot-scale work are reexamined and modeled along with data from these demonstration facilities, this will resonate in a huge way across the bioenergy community," we agree, and we intend to seek opportunities to pursue this next-step opportunity, which can greatly benefit the bioenergy community.